Exploratory Study of the Potential Airborne Health Hazard of Dusts Generated by Quarrying Volcanic Deposits

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Abstract

Occupational exposure to dust generated by quarrying siliceous rocks (i.e. sandstone, coal) is a well-documented respiratory hazard. Hazard of volcanic ash inhalation is also routinely studied (although less well understood), but the specific respiratory hazard of quarried volcanic deposits is entirely under-researched and is the focus of this study. The two main factors potentially implicated in respiratory toxicity of volcanic quarry dust are: i) crystalline silica content implicated in silicosis and lung cancer; and ii) iron-catalysed hydroxyl radical generation, implicated in inflammation and carcinogenesis. Twelve sites (in New Zealand, Montserrat and Greece), quarrying a range of volcanic deposits, were investigated and compared with volcanic ash samples (to test suitability as an analogue) and dust from non-volcanic quarries (greywacke and sandstone) in an investigation of the physicochemical characteristics which may influence particle surface reactivity. Samples of deposited dust (<1mm size fraction) were collected and 11 of these separated to ≤10μm for further analyses. Compositional analyses (XRF) showed the samples spanned the range of magmatic compositions from mafic to felsic (44-76 wt.% SiO_2). The finest material was generated by drilling lava flows (8.3-27.5 cu.vol% <10 μm diameter particles in <1mm fraction), however, several other sample types (i.e. dust on processor) contained high levels of respirable material, akin to volcanic ash from equivalent eruption settings. SEM analyses confirmed particles to be blocky and angular, having aspect ratios between 0.59-0.70 (<10μm fraction). Crystalline silica content was highest (up to 28 wt. %) in dusts from intermediate and felsic quarries where lava domes (or collapse deposits) are mined. Similar levels were observed for dome-collapse ash and greywacke quarry dusts; however, the sandstone quarry dust was 99 wt.% crystalline silica. Hydroxyl radical generation was lower for quarried volcanic samples than for either volcanic ash or sandstone (significant to $p \leq 0.01$ for mafic ash/quarry dust). Haemolysis (erythrocyte membrane rupture, an indicator of quartz reactivity) was exhibited by six samples from three quarries, and comparable to the DQ12 quartz positive standard, when adjusted for surface area. These findings may be influenced by the presence of clays, however, as haemolytic samples included those with little crystalline silica. Airborne dust levels (both role-specific and ambient) were measured in the quarries and were mostly within international exposure limits, however, interpretations were limited by the duration of measurements so further work is required. Some workers' shifts were longer than 8 hours, and workers on Montserrat may also be simultaneously exposed to volcanic ashfall, which should be considered with respect to adherence to regulations in those quarries. Mitigation measures were variable and workers would benefit from better awareness regarding use of non-mandatory respiratory protection. Volcanic quarries pose a hazard distinct from volcanic ash and from non-volcanic quarries. Overall, hazard may be lower than for quarrying other rock types, but further research is needed to better constrain the potential hazards. Until then, a precautionary approach might be taken in quarries where respirable dust levels are high and deposits may contain crystalline silica or iron.

Declaration

I declare that this thesis is re-submitted for the degree of Doctor of Philosophy at Durham University, it is my own work and not substantially the same as any which has been previously submitted at this or any other university. Where appropriate, I have clearly indicated the contributions of colleagues to fully acknowledge all collaborative work.

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Dedication

To the memories of my grandparents Jan Jakacki (1919-1964) and Helena Jakacka (née Mystkowska) (1923-2002), resistance fighters in the Polish underground Home Army and political prisoners under the Soviet regime. In honour of the truth that one can be robbed of everything except one's principles.

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Chapter 1 – Introduction

1.1 Rationale

Certain types of mineral dusts have the potential to cause adverse health effects, particularly in the mining and quarrying industries. Hippocrates first described this possibility when, in 400 B.C., he observed a lung disease associated with the breathing difficulties of men who dug for metals. In 1556, Agricola described the effects of mining-related diseases upon the lungs:

"*For the dust which is stirred and beaten up by digging penetrates into the windpipe and lungs, and produces difficulty in breathing, and the disease which the Greeks call ἀσθμα.*" (*asthma*) (Hoover & Hoover, 1950)

Silicosis (a fibrotic lung disease related to crystalline silica inhalation) was described in detail less than two centuries later by Ramazzini who was generally regarded as the 'father' of occupational medicine. The link between crystalline silica inhalation and silicosis has since been studied in detail, especially with regard to the quarrying of sedimentary rocks such as coal and sandstone (e.g.(Borm & Tran, 2002, Martin *et al.*, 1972, Reynolds *et al.*, 2003, Stone *et al.*, 2004, Weller & Ulmer, 1972, Yadav *et al.*, 2011). Crystalline silica has been listed as a human carcinogen (IARC, 1997) although its toxicity is variable (Donaldson & Borm, 1998) and its carcinogenicity to humans has not been detected in all of the industrial circumstances studied (IARC, 1997).

Rocks of volcanic origin can also contain crystalline silica (Baxter *et al.*, 1999, Merchant *et al.*, 1982) and, although these are quarried extensively, little research has been conducted on their associated dust hazard. To date, only two sites which quarry extrusive volcanic deposits have been investigated: a basalt quarry in Egypt (El Ghawabi *et al.*, 1985) and a pumice (rhyolite) quarry in Italy (Bart *et al.*, 1983, Mazziotti *et al.*, 2002, Mazziotti *et al.*, 2004). Studies at both sites reported lung disease associated with exposure to quarry dust and this highlights a key challenge in the respiratory hazard assessment of volcanic products: that volcanic quarry dust is a variable entity. Though both quarries appear to present a chronic respiratory hazard, they have very different magmatic compositions and the potentially toxic minerals and elements will therefore also differ. This thesis explores the airborne hazard of quarrying a range of volcanic deposits across the compositional spectrum of volcanic products.

When assessing hazard in a sub-discipline where little research has been conducted, it is useful to seek out potential analogue materials which have been studied in detail. Volcanic ash may potentially be used as an analogue for volcanic quarry dust, due to a common volcanic origin. Both quarry dust and volcanic ash encompass particles up to several millimetres in diameter. The term 'quarry dust' is often used interchangeably with 'quarry fines' and 'filler grade' in the extractive industry and usually refers to material ≤5mm in diameter (El-Mahllawy, 2008, Evans, 1997); whilst volcanic ash is defined as pyroclasts ≤2mm in diameter (Heiken, 1974).

Quarrying may occur in historically erupted material from a volcano which is still active (e.g. Sakurajima (Hillman *et al.*, 2012) or of recently erupted material (e.g. Merapi, Indonesia; Damby et al. 2012); therefore the quarry dust can be compared with ash from the same source. There are also many quarries which are mining ancient deposits from long-extinct volcanoes but comparison with recent, similar eruptive products may give insight into their likely hazard. Much work has been conducted on the physicochemical and toxicological characteristics of volcanic ash over the past decade (e.g.(Baxter *et al.*, 2014, Damby *et al.*, 2013, Gislason *et al.*, 2011, Hillman *et al.*, 2012, Horwell *et al.*, 2013, Horwell *et al.*, 2003, Le Blond *et al.*, 2010) and here the aim is to compare the findings from the volcanic quarries with those from analogue eruptions to assess whether ash can be used as a proxy indicator of likely respiratory hazard. Quarry dusts of non-volcanic origin will exhibit a dissimilar mineralogy to volcanic quarry dusts and therefore existing work on the exposure of quarry workers to dust may not be relevant to volcanic settings.

There are several reasons why volcanic ash may pose a potential respiratory health hazard, including: high crystalline silica content, iron-induced free radical generation and the presence of potentially harmful precipitates on ash surfaces. Concern over the potential respiratory hazard of volcanic ash gained momentum following the eruption of Mt St Helens in 1980, due to the presence of a few weight per cent (wt.%) crystalline silica in the ash (Bernstein *et al.*, 1986, Buist, 1982, Vallyathan *et al.*, 1983). More recently, iron-induced free radical generation from ash particle surfaces was postulated as another potential mechanism for respiratory toxicity (Horwell *et al.*, 2007, Horwell *et al.*, 2003). Leachate studies have also revealed the presence of volatiles and metal species on ash surfaces (adsorbed when the ash passes through plume gases

(Witham *et al.*, 2005)), which may potentially affect the respiratory system through leaching by lung fluid.

Whilst volcanic ash has been comparatively well studied (e.g.(Baxter *et al.*, 1981, Damby *et al.*, 2013, Fruchter *et al.*, 1980, Gislason *et al.*, 2011, Hillman *et al.*, 2012, Horwell *et al.*, 2013, Horwell *et al.*, 2010a, Horwell *et al.*, 2010b, Le Blond *et al.*, 2010) and may be a useful analogue in some ways, the nature of the airborne hazard represented by ash and by quarry dust could be different. Quarry dust is generated by industrial operations (Moyes & Reeves, 1974) which differ from the process of volcanic ash fragmentation (Heiken & Wohletz, 1985) and could lead to differences in size and morphology. These differences could then lead to variances in the proportions of the primary minerals in the resulting grain size fractions (Pye, 1987), even when comparing quarry dust and volcanic ash from the same volcanic source.

Given both: 1) the potential for differences between volcanic quarry dust and erupted ash, and: 2) the dearth of volcanic quarry dust health studies, there is a clear gap in knowledge regarding the specific airborne hazard of volcanic quarry dust. This is of particular concern in areas of continuing volcanic activity because workers may be exposed to quarry dust occupationally and to erupted ash environmentally, and results from this study may benefit both quarry and volcanic hazard managers.

The hazard assessment of volcanic quarry dusts studied here, centres on three key areas of investigation: 1) physical characterisation, 2) particle reactivity and 3) exposure. Physical characterisation aids in assessing which deposits are likely to be hazardous, whilst particle reactivity provides insight into the interaction of the surfaces of dust particles with cellular components, and finally determining exposure levels establishes whether a potential hazard may exist.

1.2 Aims

This project has five major aims, which combine disciplines, in order to provide a holistic assessment of the potential occupational airborne hazard posed by volcanic quarry dusts. These aims, along with a brief rationale and methodology, are presented below.

1) *To investigate the physical, mineralogical and chemical characteristics of volcanic quarry dust.*

A range of different deposit types will be studied (from solid lava through to loose ash) across the magmatic spectrum (from mafic to felsic). The following physical parameters are considered and compared: grain size (specifically proportion of <15 μm in samples), surface area, particle morphology, sample mineralogy and bulk chemistry. Determining grain size distribution is crucial because only particles small enough to penetrate the lung can potentially pose a hazard. The grain size distribution is determined using laser diffraction granulometry. Surface area is an important control of the potential surface reactivity and was measured by N_2 gas adsorption using the Brunauer Emmett Teller theory isotherm method. Morphology is a key characteristic because certain morphologies (i.e. fibres and plates (Burragato *et al.*, 2005, Deng *et al.*, 2012, McDonald *et al.*, 2004)) present greater difficulty for lung clearance; morphology was appraised qualitatively using scanning electron microscopy and image analysis. Mineralogical characterisation focuses on the minerals of chief health concern, specifically the crystalline silica polymorphs, which are implicated in the instigation of multiple lung diseases (Donaldson & Borm, 1998, Duffin *et al.*, 2001, IARC, 1997, Pelucchi *et al.*, 2006). The polymorphs were identified semi-quantitatively using the internal attenuation standard (IAS) method of X-ray diffraction with static position sensitive detection (Le Blond *et al.*, 2009). The bulk chemical characterisation of quarry dusts enables classification by magmatic type, which is important in informing the likely mineralogy (including iron-bearing minerals and crystalline silica polymorphs), and was determined by X-ray fluorescence.

2) *To determine the surface reactivity and potential toxicity of volcanic quarry dust.*

Whilst physical, mineralogical and chemical characterisation is important, it reveals only part of the potential airborne hazard; the additional incorporation of surface reactivity

and toxicity tests provides a deeper understanding of the quarry dust hazard. Iron-induced hydroxyl radical generation is one manifestation of surface reactivity which can lead to lung inflammation and is a carcinogenic factor (Fubini & Otero-Areán, 1999). Surface iron available for reaction was determined spectrophotometrically by chelation, and radical generation was measured by electron paramagnetic resonance spectroscopy. Potential toxicity was determined by investigating the reactions of particles with cellular membranes, this was assessed through the haemolysis assay.

3) *To examine exposure to dust in volcanic quarries.*

Exposure to the health-pertinent fractions of dust was measured in the field with real-time monitors. A DustTrak™ aerosol monitor was used to measure the ambient levels of dust in different parts of a quarry and a SidePak™ aerosol monitor was used to determine personal exposure of workers in different roles within quarries. This is an important parameter because increased exposure impedes clearance from the lungs and increases the potential for morbidity, whilst a lack of exposure implies little potential for risk (Hemenway *et al.*, 1990, Kreyling *et al.*, 2007).

The likelihood of workers complying with exposure mitigation is influenced by their perception of dust as a risk, so the evaluation of exposure was further supported through in-field ethnographic observations and a pilot study on risk perception by the quarry workers.

4) *To assess how the occupational hazard of quarrying volcanic deposits differs from environmental exposure to volcanic ash.*

A suite of specially selected volcanic ash samples is analysed alongside the quarry dusts for most of the characterisation and toxicity tests presented above. Volcanic ash has been well studied and its suitability as an analogous material for volcanic quarry dust will be investigated; however, the occupational hazard of dust inhalation is likely to differ from exposure to freshly erupted volcanic material. A greater understanding of the similarities and differences between these exposures could inform the work of hazard managers in both arenas.

5) *To integrate interdisciplinary techniques to provide a holistic appraisal of the potential dust hazard during quarrying.*

The findings from aims 1-3 are combined, highlighting the benefit of an interdisciplinary approach. This type of methodology need not necessarily be restricted to volcanic deposits; to illustrate this, samples from non-volcanic quarries are analysed for comparison.

1.3 Structure

This thesis is comprised of eight chapters; a brief overview of the remaining chapters is given below.

Chapter 2 comprises an introduction to the quarrying industry and associated dust-producing activities, and an overview of the fields (toxicological, epidemiological, clinical and mineralogical) related to both quarry dust and volcanic ash exposure. The biological mechanisms of mineral-related disease are reviewed along with factors pertaining to the surface reactivity of dust particles.

Chapter 3 provides a background to the geology of the field sites visited as part of this study and details the sample collection protocols undertaken in the field.

Chapter 4 investigates important physical, mineralogical and chemical characteristics in relation to the potential airborne health hazard of the dust as detailed in *aim 1*. These parameters are compared with those from a suite of volcanic ash samples and samples of non-volcanic quarry dust (*aim 4)*.

Chapter 5 investigates the surface reactivity and potential toxicity of volcanic quarry dust, through chemical and cellular tests as described in *aim 2*. Again, comparisons are drawn between the results of different tests and types of dust studied (*aim 4*).

Chapter 6 evaluates the exposure to dust in volcanic quarries as outlined in *aim 3*. This pilot study examines the exposure of different quarry roles to the health-pertinent dust fractions. The actions of quarry workers in relation to mitigating their exposure are also explored through a small-scale ethnographic study and associated qualitative questionnaires (the latter feature in Appendix IV).

Chapter 7 synthesises the results from chapters 4-6, as outlined in *aim 5*, through the comparison of different health-relevant parameters. A qualitative ranking of the potential health impact based upon surface reactivity and toxicity is presented in an attempt to determine whether physical, mineralogical and chemical parameters influence the exhibited reactivity and toxicity.

Chapter 8 summarises the main findings of the study in relation to the aims outlined above. It appraises the wider context of the study in relation to the quarrying of other mixed dusts and makes suggestions for aspects which require further study.

Appendix I contains details of each of the quarries visited as part of this study (supplementary to Chapter 3).

Appendix II contains supplementary material for Chapter 4.

Appendix III contains supplementary material for Chapter 5.

Appendix IV contains supplementary material for Chapter 6, including questionnaires for the pilot study of risk perception and the associated ethical documentation.

Appendix V comprises papers relating to eruptions at Chaitén (Horwell *et al.*, 2008) and Rabaul (Le Blond *et al.*, 2010) to which the author contributed.

1.4 Approaches and Scope

This large study attempts to characterise samples across the magmatic spectrum and inevitably certain assumptions are required in relation to both the samples and their analysis. There are four limiting assumptions within this study which require consideration: 1) the size fraction utilised for analyses, 2) the comparability of samples (both in terms of sample age and the differing environments from which they were collected), 3) the use of non-reactivated dust and 4) the impacts of seasonal climate variation. The data collected are appraised with these assumptions in mind.

1.4.1 Size fraction

Respiratory *in vitro* and *in vivo* toxicology studies on environmental particulate matter are routinely conducted on lung-pertinent size fractions (either PM10 or PM4) (Kelly & Mudway, 2007, Reynolds *et al.*, 2003, Vallyathan *et al.*, 1992, Vallyathan *et al.*, 1983, Wilson *et al.*, 2000), where size-selected airborne particulate has been collected on filters (e.g. using a cascade impactor), or separated from the bulk sample using elutriation techniques (Jones & BeruBe, 2011). These methods of particle collection generate samples of a few mg which is a quantity sufficient for toxicology assays only unless a high-volume impactor is used (which is impractical for the majority of field studies), or an industrial separator (which involves critical loss of sample within the separator(Horwell, 2002)). This study focuses on physical, chemical and mineralogical analyses, in order to fully characterise the deposits at each quarry in terms of their potentially toxic characteristics; such analyses require a total of ~15g of sample, therefore the use of filter-collected particulate is precluded. Where possible, the health-pertinent fractions are studied: the amount of health-pertinent particulate in the bulk sample is calculated by laser diffraction, and for morphology (by SEM) only thoracic (<10 µm) particles are analysed; but for all analyses, except haemolysis and some crystalline silica quantification, the amount of sample required for each analysis precluded using a separated fraction of <10 µm.

This approach was essential for successful particle characterisation; however, it is acknowledged that some results, such as surface area or hydroxyl radical generation, may not accurately reflect those that would have been obtained for the respirable or thoracic fractions. This is an on-going problem in the particle toxicology field and insufficient material for full characterisation is responsible for the poor physicochemical characterisation within toxicology studies (Horwell, 2011). The only exception is for manufactured particles (e.g. man-made nanoparticles) where sufficient material for a full characterisation can be produced. Until techniques are readily available for rapid, accurate separation of bulk particulate samples, or more practicable collection of lung-pertinent airborne samples, the structure-toxicity relationship will continue to be only loosely addressed in most particle toxicology studies.

For this study, however, the physicochemical characteristics of the deposits were the focus and therefore a <1mm fraction sieved from bulk material is used throughout.

Sufficient <10 µm material was separated for haemolysis of highly-reactive samples (tested first as bulk samples) and limited XRD analysis. This use of the <1mm fraction has the advantage of being directly comparable to a range of recent studies on volcanic ash that make use of a novel protocol recently developed by the International Volcanic Health Hazard Network (Horwell, 2013) to assess the respiratory hazard posed by ash inhalation. This protocol was implemented on the <1mm fraction for eruptions at Chaitén (Horwell *et al.*, 2008) and Rabaul (Le Blond *et al.*, 2010) to which the author contributed (see Appendix V); and also at Merapi, Sakurajima, Eyjafjallajökull and Grimsvötn (Damby *et al.*, 2013, Hillman *et al.*, 2012, Horwell *et al.*, 2013). This interdisciplinary protocol allows for broader characterisation and investigation of dust toxicity than cellular testing on the respirable fraction alone. There is also a precedent for using coarser fractions (such as <1mm) in studies on non-volcanic quarry dust (Petavratzi *et al.*, 2007).

Although the use of the <1mm fraction for physicochemical characterisation clearly has its limitations, this fraction can, however, contain high levels of inhalable material. A study of dustiness in British limestone quarries involving simulated quarry operations found that, in simulations using the <1mm fraction, the dust generated contained up to 80 cumulative per cent (cu.%) <10µm material and 25cu% <2.5µm material (Petavratzi *et al.*, 2007). The study also found that differing operational procedures did not greatly influence the size profile of the dust; therefore, collection of bulk dust and subsequent separation of the <1mm fraction from different areas of the quarry, would be fairly representative in this case. This is important because the quantity of bulk dust collected often needs to be on the order of several hundred grams in order to ensure enough of the <1mm fraction can be separated for characterisation, which introduces a constraint in respect to the number of samples which can be feasibly collected within a quarry.

Mineralogy can differ between different grain sizes of dust. A study into the dustiness of quarry operations at an Iranian marble quarry found differences in quartz content when comparing the respirable and total dust fractions (Golbabaei *et al.*, 2004). Furthermore, the proportions do not remain uniform between the two size fractions when comparing across different quarry operations: workers using the cutting machine and bulldozer were exposed to the highest proportion of quartz in the respirable fraction, whereas hammer drill operators were exposed to the highest proportion of quartz in the

total dust. Studies of aeolian dust separated into lung-pertinent size fractions (<2µm, 2-5µm and >5µm) revealed that the coarser fractions contained greater quantities of quartz and plagioclase (by XRD) in comparison to the finer fractions which were comparatively enriched in smectites, kaolinite, micas, and chlorite (Prospero & Bonatti, 1969). To investigate these issues in the present study, analysis of crystalline silica content is conducted on several different samples collected from different locations within each quarry as well as being repeated on some samples of the separated <10µm fraction. The results from bulk material compared to the <10µm fraction are considered when interpreting data in chapters 4 and 5.

Toxicity studies on volcanic ash have mainly focussed on the respirable fraction, with the exception of those carried out using the IVHHN protocol (see above). One recent study compared haemolysis for both the <1mm fraction and the separated respirable fraction at five different volcanoes (Damby, 2012). Overall levels of haemolysis were found to be low and no clear relationship between particle fractions and haemolytic activity was observed. For some samples, the respirable fraction was several times more haemolytic, whereas in others there was little difference (see Chapter 5, Section 5.5) (Damby, 2012). A study of diatomaceous earth also investigated haemolysis for the <1mm fraction alongside the separated respirable fraction and found no significant statistical difference (t-test with ANOVA) (Nattrass, In prep.).

It is difficult to discern with precision, therefore, the likely differences in physicochemical characterisation between the respirable dust and the <1mm fraction. The first stage of the physicochemical analyses (Chapter 4), therefore, appraises the proportions of the health-pertinent material within the <1mm samples (by laser diffraction grain size analysis) and only those with elevated levels of <100µm (inhalable) material were selected for further characterization. Whilst mass will still be dominated by larger particles, such selection (based on <100µm content) ensures that the study's results are of most relevance to assessing the airborne hazard.

1.4.2 Sample Comparability

This study investigates the dust hazard at 11 volcanic quarries and two non-volcanic quarries. The countries visited were: New Zealand, Greece and Montserrat, the latter is volcanically active, thereby presenting a unique opportunity to sample an area where both occupational and environmental exposure occurs.

Whilst using a range of sites facilitates the development of broader implications for the hazard of volcanic quarrying, this variability also limits the opportunity for direct comparisons to be drawn, making it difficult to determine the impacts of variability both in the ages of the deposits and their respective environments.

Some quarry sites, particularly older deposits (such as in New Zealand and Greece), may be more affected by weathering (for example through the percolation of water), whereas recently erupted deposits (such as on Montserrat) will be less affected. Further, post-extraction, dust will experience different residence times in the environment; for example, dust from freshly extracted material compared to dust accumulated on the processor or in the stockpile. One of the key constraints of environmental residence time (post-extraction) is the level of turnover of material in the quarry; the busiest quarries in New Zealand clear all stockpiles typically within a fortnight, whereas the quarries on Montserrat sell material which was quarried 2-3 months previously due to the economic impact of the on-going eruption. Dust with a longer environmental residence time is likely to have been exposed to rain and may have undergone leaching, which is likely to affect its surface chemistry (Ayris *et al.*, 2013, DelMelle *et al.*, 2007).

Dusts with very fresh surfaces have potentially higher surface reactivity than their aged or weathered counterparts. A study on freshly milled crystalline silica in comparison to aged crystalline silica, found that fresh samples generated significantly more free radicals, enhanced lung injury and resulted in greater inflammation (Vallyathan *et al.*, 1995). Experiments on freshly ground volcanic ash have shown that grinding increased the surface reactivity (hydroxyl radical generation) for bulk samples (in comparison to their non-ground counterparts) but did not, however, appreciably alter reactivity for the respirable fraction (Horwell et al., 2003). Whilst grinding in the laboratory has the potential to produce particulate more analogous to freshly generated dusts, the grinding itself may lead to changes in the particle, especially regarding particle size, shape and

surface area, which could also have an effect on reactivity and comes with its own limitations.

Sample surfaces were not refreshed by grinding in this study, with the exception of one haemolysis assay on the re-ground <10 μm separated fraction. Further analyses were not conducted on re-ground material for two key reasons: 1) grinding is not completely representative of the various modes of dust generation in a quarry and 2) freshly ground dust is not representative of the full range of dust conditions to which workers are exposed. In the quarrying industry, a rolling drum test method has been developed to mimic dust generation, as continuous rolling was found to best simulate dust production from the materials handling process (Breum, 1999, Petavratzi *et al.*, 2007) as opposed to grinding. Furthermore, the exposure to fresh surfaces is only likely to occur if a worker is near the processor whilst material is being processed, or nearby during extraction of raw material, particularly during blasting. These are comparatively rare scenarios (workers carrying out extraction are typically protected by an air-conditioned cab) because, even after blasting, workers in New Zealand are advised to wait (varying between one hour and one day) before processing newly-blasted material in case of any unexpected land movements. It has been found that heightened reactivity resulting from freshly crushed silica surfaces begins to tail off over a timescale on the order of hours, with hydroxyl radicals exhibiting a half-life of ~20 hours (Vallyathan *et al.*, 1995, Vallyathan *et al.*, 1988) therefore using samples collected in the field (without regrinding) is more representative of typical exposure. The use of laboratory re-ground samples is suggested as a potential area of interest in the further work section of the concluding chapter.

1.4.3 Weather and climate variability

Weather patterns are known to affect the emission rate of dust in quarries (Chang-Tang, 2004), with dry or windy conditions particularly problematic for dust control (Petavratzi et al., 2007). Dust assessments conducted at two different limestone quarries found that more dust was naturally produced during the dry summer season compared to other times of the year (Bluvshtein *et al.*, 2011), and that wetter dust deposits out of the air shortly after formation (Vella and Camilleri, 2005). As wet particles are heavier and tend to aggregate and fall out of the air more rapidly, rain decreases the dustiness of the air

and the use of water as a means of dust suppression is also commonly implemented in quarries (Cotes & Steele, 1987). Furthermore, mechanical fracturing in a dry atmosphere cleaves Si–O bonds leading to very reactive surface species, whereas, fracturing in the presence of water vapour leads to the formation of surface SiOH species instead (Fubini & Otero-Areán, 1999).

Seasonality and associated weather, will therefore impact dust levels in a quarry, and is an important consideration in hazard assessment. Furthermore, the geographic environments of each quarry site also differ (for example, altitude, elevation and surrounding vegetation type) which combined with the weather and the moisture content of the rock, will affect the quantities of dust produced (Chang-Tang, 2004).

In light of this, and given that only one trip to each location was feasible, the fieldtrips were designed to occur during the drier (and less windy) times of year, to provide a more 'averaged' picture; i.e. not during the wet season when dustiness will be lowest, but also not during periods of dryness with high winds, when dust levels will be most elevated. In New Zealand, the late summer and early autumn period was chosen, and on Montserrat the post-hurricane summer season. The climate of Greece is comparatively dry and warm; however, the summer season was also selected to provide greater comparability. The weather conditions during field seasons were noted as well as the use of water for dust suppression; therefore, the possibility of influence from wet weather or suppression techniques can be highlighted.

It is very likely, however, that the dust levels during the hurricane season (on Montserrat) or in winter (in New Zealand) would have yielded a different exposure hazard; this should be considered when designing longer-term monitoring plans.

It is important to note, therefore, that the data presented here are a 'snapshot' of particular quarries and conditions during a particular point in time and are not representative of all possible conditions and all seasons.

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Chapter 2 – Quarried Volcanic Particulate and Respiratory Disease: An Overview

2.1 Introduction

Previous work on the health effects of quarry dust has focused on siliceous sedimentary rocks (e.g. sandstone, diatomaceous earth (Checkoway *et al.*, 1997, IARC., 1997, Pelucchi *et al.*, 2006, Rushton, 2007)) and intrusive igneous rocks (e.g. granite (Ahlmark *et al.*, 1965, Koskela *et al.*, 1987, Olusegun *et al.*, 2009)). Investigations into the potential respiratory health effects following exposure to volcanic ash have highlighted two specific characteristics influencing the potential toxicity of volcanic particles: crystalline silica (Baxter *et al.*, 1999, Forbes *et al.*, 2003, Hincks *et al.*, 2006) and reactive iron on particle surfaces (Horwell *et al.*, 2007, Horwell *et al.*, 2003). Both of these characteristics have been investigated for recent volcanic eruptions in Chile (Horwell *et al.*, 2010a), Papua New Guinea (Le Blond *et al.*, 2010), Indonesia (Damby *et al.*, 2012), Japan (Hillman *et al.*, 2012) and Iceland (Horwell *et al.*, 2013a). In addition, only two sites which quarry volcanic deposits have been investigated for their dust hazard and associated disease patterns (El Ghawabi *et al.*, 1985, Mazziotti *et al.*, 2002, Mazziotti *et al.*, 2004).

This chapter contains a review of dust generation in quarries, the diseases associated with quarrying and volcanic ash, the consequences of inhaling particulate (both the fate of the particles and associated disease endpoints), the factors which control the toxicity of mineral particulate, and finally summarises key methodologies for evaluating dust exposure.

2.2 Quarrying Volcanic Deposits and Dust Generation

The quarrying of volcanic material occurs on a global scale, often in volcanically active regions. Differing magma types and eruptive styles result in a broad range of volcanic products which have distinct industrial applications. The processes of extraction, processing and distribution of finished product varies among quarries depending on the type of deposit, however, all of these activities have the potential to produce dust.

2.2.1 Quarrying volcanic deposits

It is difficult to estimate the numbers of people involved in (or even affected by) volcanic quarrying specifically, as there are no published statistics for this particular category. In 2006, in the EU, 288,500 were employed in the extraction of non-energy-producing materials (E.U. Commission, 2009). In the USA that figure was 216,200 in June 2012 (U.S. Department of Labor Bureau of Labor Statistics, 2012). In Australia in 2001, 7,500 people were employed in aggregate quarrying (Institute of Quarrying Australia, 2012). Volcanic quarries exist in a variety of locations around the world. Some examples include: Italy (Sicily, Phlegrean Fields, Lipari), Turkey, Greece (Santorini, Milos, Yali), Indonesia (Merapi), New Zealand (various, North Island), Canada (Quesnel, British Columbia, is the largest volcanic quarry in North America), USA, Montserrat, West Indies, India and Japan. There are a wide variety of uses for quarried volcanic materials, summarised in Table 2.1 below.

Table 2.1 The types of volcanic deposit quarried, their special properties and associated uses. After: Heiken (2005), United States Geological Survey (2012) and Winstone Aggregates (2012)

Deposit Type	Application and any Special Properties
Trachy-basalt Basalt	Road aggregate, drainage, bulkfill, landscaping, farm maintenance.
Andesite	Concrete admixture and aggregate, construction building blocks.
Pumice	Construction building blocks, horticulture (highly porous; useful for drainage), abrasives, concrete admixture and aggregate, absorbent, filtration (highly porous), laundry stone washing (i.e. stone-washed jeans, due to abrasiveness).
Perlite	Building construction products, fillers, horticultural aggregate, filter aid (when heated above 871^{o}C perlite expands to 4-20 times its original volume).
Obsidian	Sub-base for roads and building foundations, surgical instruments (due to propensity to conchoidal fracturing, hardness and sharp clean edges when cut).

Non-volcanic rocks can also be used for construction and road aggregate purposes and are not treated as a separate category (to materials of volcanic origin) in production figures, therefore it is difficult to estimate the likely production levels of quarry materials from mafic and intermediate deposits. Felsic deposits such as pumice,

pumicite (finer-grained pumice) and perlite are used for more specialised applications and statistics on global production are recorded by the US Geological Survey (USGS), these values are shown in Table 2.2.

Table 2.2 World production of pumice and perlite, and usage statistics in the USA. Figures are shown in thousands of metric tonnes (kmt). Adapted from USGS Minerals Fact Sheet, 2012 (United States Geological Survey, 2012).

Mineral	2011 Total global production (kmt)	Top three producers (kmt)	Use in USA (% of total use)
Pumice and Pumicite	17,000	Turkey (4,100) Italy (3,000) Greece (1,300)	Construction building blocks (70%) Horticulture (16%) Abrasives (6%) Concrete admixture and aggregate (4%) Absorbent, filtration, laundry stone washing (4%)
Perlite	1,900	Greece (500) Turkey (500) USA (400)	Building construction products (55%) Fillers (14%) Horticultural aggregate (14%) Filter aid (9%) Unknown (8%)

2.2.2 Dust generation in quarries

The exact nature of extraction and processing of rock varies from deposit to deposit; however, the general quarrying process is much the same at any site. Figure 2.1 illustrates the general features within a quarry. Material is extracted from the deposit and processed by crushing and/or size screening, and then it is stockpiled ready for sale or exportation.

Figure 2.1 The typical components of a quarry (Phoenix quarry, Little Bay, Montserrat).

Dust in quarries is created by tearing, breaking, blasting, sawing, drilling, crushing, grinding, sanding, filing, or otherwise abrading a material (Cotes & Steele, 1987). A variety of methods exist to reduce levels of respirable dust including: suppression, collection, containment (Health and Safety Executive, 2008), and education and inspection (Cotes & Steele, 1987). Despite these methods, occupational respiratory diseases still persist, with 300 deaths from silicosis annually in the USA alone (World Health Organization, 2000).

2.3 Quarrying and Human Health

2.3.1 Volcanic Deposits

To date, in this small field, two diseases have been identified as resulting directly from exposure to quarried volcanic particulate. At the mafic end of the magmatic spectrum, basalt pneumoconiosis has been identified from a crushing plant in Egypt (El Ghawabi *et al.*, 1985), and at the felsic end, liparitosis (another form of pneumoconiosis) has been discovered amongst workers quarrying pumice on the island of Lipari, Italy (Mazziotti *et al.*, 2002, Mazziotti *et al.*, 2004). The pneumoconioses are a suite of lung diseases characterised by the formation of fibrotic tissue associated with dust exposure. The exact pathology depends on the type of dust inhaled.

Basalt quarries are commonplace worldwide, particularly in the large igneous provinces (LIPs), such as the Deccan Trapps (India) or the Columbia River Basalts (USA). The predominant minerals in basalt are: olivine, pyroxene, and plagioclase, in addition to volcanic glass, none of which are individually known to have respiratory toxicities (Jones & Berube, 2007) (see Sections 2.6.3 and 2.6.4). A study of the health of workers who crushed basalt extracted from a lava flow in Abu-Zaabal, Egypt revealed 28 cases of basalt pneumoconiosis (27% of the workforce) based on diagnoses by chest radiographs (El Ghawabi *et al.*, 1985). Furthermore, chronic bronchitis was more prevalent amongst the quarry workers in comparison to the control group (who had never been exposed to dust occupationally). The duration of employment at the plant had a statistically significant effect on the lung function of the workers, although there was no correlation between these data and the individual roles of the workers (foremen, maintenance workers, crusher operatives, truck drivers etc.) (El Ghawabi *et al.*, 1985). The authors found that 3.3% of the respirable dust consisted of crystalline silica, which is the mineral of principal health concern (see Section 2.6.3). Following the determination of silica levels in the dust, the hazard was described as silicotic (capable of instigating the pneumoconiosis silicosis), resulting from crystalline silica exposure (El Ghawabi *et al.*, 1985). Basalt typically only contains <5% quartz (MacDonald, 1972), so volcanic ash studies have focused on the iron-catalysed free radical generating potential of basaltic ash (see Section 2.6.4). It is not

clear from this study whether the 'basalt pneumoconiosis' observed in the workers is truly different from other types of mixed dust pneumoconioses or from silicosis, and it is not confirmed whether crystalline silica instigated the pneumoconiosis.

Rhyolitic pumice quarries are found predominantly in the Aegean, the USA and Japan (United States Geological Survey, 2012). Liparitosis is a distinct pneumoconiosis with a latency period of 20 – 30 years, characterized by progression from a fine reticulation (emerging network of connective tissue) to a later stage mass-like fibrosis (Castronovo, 1953). The pumice of Lipari is glassy but contains an appreciable amount of crystalline silica (1.2-5wt.% (Jones & Berube, 2007)) often perlitic and as rare, small microphenocrysts (10-50µm) (Acquafredda & Paglionico, 2004). Liparitosis appears to have a distinct pathology from silicosis, being first defined in 1953 by Castronovo on the basis of chest radiography (Castronovo, 1953). More recently (2002) a study of two Lipari quarry workers who exhibited symptoms of liparitosis, revealed the presence of pleural lesions by high-resolution computed tomography (HRCT) (Mazziotti *et al.*, 2002). This led to a further study, which identified 31 workers who were subject to annual tomography investigation; three workers exhibited lung masses, whilst HRCT revealed pleural plaques in eight cases. The study found that pleural opacities are observed in workers, but those exposed to heated pumice (prior to technological innovations at the quarry) exhibited greater disease progression (Mazziotti *et al.*, 2004) which may have resulted from the crystallisation of silica during the previous practice of pumice heating and desiccation. Amorphous silica has typically been found to be less fibrogenic than its crystalline counterparts in toxicological investigations (IARC., 1997, Reuzel *et al.*, 1991), however, there are very few studies which have determined the highly variable amorphous forms of silica (which range from those that are poorly characterised to synthetically produced forms) and the reasons for varying toxicity between crystalline and amorphous forms are not fully understood (Fubini *et al.*, 2001, Ghiazza *et al.*, 2010, Warheit, 2001).

2.3.2 Non-Volcanic Deposits

There are several lung diseases which humans may develop following exposure to mineral dusts, particularly in occupational settings such as quarries and mines. Broadly, acute diseases such as bronchitis and asthma are instigated by particles of the 'thoracic' fraction (<10µm diameter), in the upper airways, whereas the 'respirable' fraction (<4µm diameter) is implicated in chronic diseases, including silicosis and cancer, in the deep lungs (Beckett, 2000a) (see Section 2.6.1 for description of these fractions). Diseases associated with quarry dust exposure include: silicosis, mixed dust pneumoconiosis, silico-tuberculosis, chronic obstructive pulmonary disease (COPD) and lung cancer and are briefly described below.

Silicosis

Where dusts contain in excess of ~10 wt.% crystalline silica, there is a risk of developing silicosis amongst workers (Buchanan *et al.*, 2003). There are three key factors which determine the type and progression of silicosis: cumulative exposure, intensity of exposure, and latency. The key characteristic of silicosis is the development of silicotic nodules in the lungs as the body tries to isolate silica particles from sensitive tissue (Dart, 1946, Green & Vallyathan, 1996, King, 1947). Radiographic studies (chest X-rays) have revealed that silicosis can progress even after exposure has ceased, which highlights the need to minimise occupational exposure. The mechanism(s) responsible for silica toxicity are not well-constrained and there are a number of possible molecular pathways for silica toxicity (see Section 2.6 for factors influencing toxicity). It is thought, however, that no single property of crystalline silica controls its disease-causing potential (Fubini, 1998, IARC., 1997).

Research into the pathogenesis of silicosis has focused, therefore, on four main areas:

i) Physical and chemical properties of silica particles
ii) Deposition, clearance and retention of silica particles
iii) Interaction of silica particles with cell membranes, cells, tissues and organs

iv) Cellular and humoral (body fluids) responses associated with disease and disease progression (Green & Vallyathan, 1996).

Silicosis manifests itself in various forms. *Acute Silicosis* (silicolipoproteinosis) is a rapidly progressive form with a high mortality rate. It develops following intense exposure, sometimes after as little as six months. *Accelerated Silicosis* is linked to high to moderately intense exposure, with a latency period (time between exposure to silica dust and when symptoms first appear) of 1 to 14 years. *Chronic Simple Silicosis* is the most prevalent lung disease linked to crystalline silica inhalation. Low exposure can lead to a latency period on the order of decades, after which the disease may progress slowly over many years (Green & Vallyathan, 1996, Harley & Vallyathan, 1996, World Health Organization, 2000). Siderosis (a simple pneumoconiosis caused by inhalation of iron oxide (Cotran *et al.*, 1998)) can occur as a result of quarry iron bearing ores, e.g. haematite, limonite and magnetic pyrite; where the ore contains quartz and silicosis is also present, the conditions may merge into *sidero-silicosis* (Cotes & Steele, 1987). Progressive massive fibrosis (PMF) is a large fibrotic lesion which is distinguished from the 'classic' silicic nodule on the basis of its size but is associated with silicosis (Green & Vallyathan, 1996).

Occupational exposure to silica dust has a long history, with the first mining activities taking place in China, India and Egypt in around 4000 BC (Harley & Vallyathan, 1996). In modern times, there are a variety of occupations where workers are commonly exposed to dusts containing crystalline silica and therefore potentially at risk from silicosis, these are listed overleaf in Table 2.3. The worst industrial disaster in the U.S.A. occurred during the Great Depression, when many migrant workers came to West Virginia to drill tunnels for the Hawk's Nest hydroelectric power plant (Cherniack, 1986). The workers were ordered to carry out dry drilling because it was three times faster than wet drilling, despite being extremely dusty (Cherniack, 1986). This led to an epidemic of respiratory problems which were later identified as silicosis related to the drilling of rock which was discovered to be comprised of almost pure silica (Cherniack, 1986, Greenberg *et al.*, 2007). Conservative estimates place the number of resultant deaths at 400 (Greenberg *et al.*, 2007); whilst others consider the real figure to be nearer 700 (Cherniack, 1986, Cohen *et al.*, 2008).

Table 2.3 The Occupational Exposure to Silica after Mauderly et al., (2000) with additional details from IARC monograph (1997).

Occupations and Industries at Risk from Silicosis
Quarrying, mining and stone shaping (especially sandstone, diatomite, granite and slate).
Mining of metals (notably tin, haematite, graphite, copper and gold)
Pottery industry
Manufacture of refractory products (e.g. silica bricks)
Flint crushing
Production of synthetic silica and silica milling
Millstone dressing
Manufacture of abrasive soaps
Iron and steel foundries
Sandblasting
Boiler scaling
Coal Mining
Vitreous enamelling industry
Glass polishing
Gem polishing

A historical cohort mortality study was carried out on 2,342 male workers exposed to crystalline silica (commonly cristobalite) in a diatomaceous earth mining and processing plant (Checkoway *et al.*, 1997). Excess mortality was detected for non-malignant respiratory diseases during the study period (1942-1994). It was found that with a 15-year latency period mortality rose sharply with cumulative exposure to crystalline silica. A less significant link was established for lung cancer (Checkoway *et al.*, 1997). Studies into silicosis of granite workers have been conducted for almost a century (Bloomfield & Dreesen, 1934, Rogers, 1932). A recent cross-sectional study in the USA by Rego et al. (2008) of 440 granite quarry workers revealed that 17.5% have silicosis(Rego *et al.*, 2008). Those who were exposed to silica dusts and also smoked fared worst in the spirometry (lung function) tests; however, those who did not smoke but were exposed to

silica dusts also recorded lower spirometry results compared to the control group (Rego *et al.*, 2008).

Mixed Dust Pneumoconiosis

Mixed dust pneumoconiosis describes a type of nodular fibrosis caused by silica which is inhaled in combination with less fibrogenic dusts, for example iron oxides or silicates (Green & Vallyathan, 1996). Pneumoconiosis amongst those working in quarrying and mining is thought to have been first described by Hippocrates in around 400 BC, who recorded that the men had difficulty breathing (Harley & Vallyathan, 1996). More recently, mixed dust pneumoconiosis has been investigated amongst coal miners, as coal mine dust usually contains up to 10% quartz, often within a carbon matrix, which impacts upon its surface toxicity (Borm, 1997). The development and severity of coal workers pneumoconiosis (CWP) is directly related to both duration and concentration of dust exposure (Laney *et al.*, 2012). Chest radiography of surface coal mine workers in 16 States in the U.S.A. revealed that of those who had ≥ 1 year experience, 2% were suffering from CWP and 0.5% were suffering from CWP with progressive massive fibrosis (PMF) (Laney *et al.*, 2012). The National Study of Coal Workers' Pneumoconiosis (NSCWP) is a large, on-going epidemiologic study of the respiratory health of U.S. coal miners (Attfield & Morring, 1992). Recent investigations have found that the overall prevalence of coal workers' pneumoconiosis among underground coal miners in the United States was 11.2% in 1970–1974 and 3.3% in 2005–2006, with 2-12% of miners exposed to 2mg/$m^3$of coal dust expected to have Category 2 or greater CWP after a 40-yr working life; PMF would be expected for 1.3-6.7% of workers (Attfield & Kuempel, 2008, Attfield & Morring, 1992).

Silico-tuberculosis

Pulmonary and extra-pulmonary tuberculosis (TB) are common complications of silicosis (Green & Vallyathan, 1996, Rees & Murray, 2007) and occasionally misdiagnoses occur between early-stage silico-TB and PMF (Ng & Chan, 1991). Tuberculosis is the world's leading cause of death from a single infectious disease, annually claiming 2.5 million lives (Kumar & Clark, 2009). It is a chronic bacterial disease caused by the pathogen

Mycobacterium tuberculosis (Kumar & Clark, 2009). The tendency of mycobacteria to infect silicotic lungs is not reserved to *M. tuberculosis,* however; other strains include *M. avium-intracellulare*, *M. scrofulaceum*, and *M.kansasii* (Green & Vallyathan, 1996).

The increased risk of TB for silicosis sufferers is life-long, even after exposure ends (Cowie, 1994). A cohort study of gold miners in South Africa over seven years revealed that workers with chronic simple silicosis were at almost three times greater risk of developing TB than their co-workers who, at the start of the study, had no radiographic signs of silicosis (Cowie, 1994). A review of death certificate based mortality data amongst 200 male whetstone cutters was conducted for the period 1955–1995, calculating standardised mortality ratios in reference to the health statistics of Kyoto (as a control group) where the cohort lived. The study found that of the 99 men who had died during the observation period, 10 deaths were of lung tuberculosis (9 cases of which also had silicosis), 20 resulted from 'all malignancies' and 6 died from lung cancer (Ogawa *et al.*, 2003).

Chronic Obstructive Pulmonary Disease (COPD)

COPD is a disease which is characterised by airflow obstruction due either to chronic bronchitis or emphysema, which leads to a progressive and permanent reduction of the maximum expiratory flow (Hnizdo & Vallyathan, 2003). Epidemiological studies have linked silica dust exposure to airflow obstruction both in the presence and in the absence of radiological signs of silicosis (Hnizdo & Vallyathan, 2003, Rushton, 2007). Death certificate data from 27 states of the U.S.A. from the National Occupational Mortality Surveillance database showed that those hypothesised to have detectable crystalline silica exposure had a significantly increased risk of developing silicosis, COPD, pulmonary TB and rheumatoid arthritis (Calvert *et al.*, 2003). Those with consistently increased mortality odds ratios for COPD occurred in the 'medium' and 'higher' crystalline silica exposure categories, lending evidence to support the association of COPD and crystalline silica exposure (Calvert *et al.*, 2003). A review of epidemiological and pathological evidence suggests that regular exposure to silica dust that does not instigate silicosis may lead to the development of chronic bronchitis, emphysema, and/or small airways disease,

which can result in airflow obstruction, even in the absence of radiologically confirmed silicosis (Hnizdo & Vallyathan, 2003, Rushton, 2007).

Lung Cancer

The relationship between silicosis and lung cancer is controversial and not fully resolved (Green & Vallyathan, 1996). The crystalline silica polymorphs are listed as Group 1 human carcinogens (the highest rating) by the International Agency for Research on Cancer who concluded that, in occupational settings, it is a lung carcinogen (IARC, 1997). This listing has, however, met with some criticism as re-appraisals of the same exposure-response data found a weak association (statistically) between silicosis and lung cancer (Gamble, 2011). Some authors believe that silica-induced lung cancer can only exist simultaneously with silicosis and does not develop in its absence (IARC, 1997). In mixed dust, in addition to silica, lung cancer could potentially be caused by iron-catalysed hydroxyl free radical generation as radicals have the propensity to remove electrons from DNA, causing cell mutations which may lead to cancer (Checkoway *et al.*, 1997, Hardy & Aust, 1995, Kane *et al.*, 1996). A retrospective cohort study of 1,026 granite workers in Finland employed during 1940-1981, revealed their excess cancer mortality in comparison to the control group which comprised the general Finnish male population in the (median) year 1972. The study showed that 22 cases of lung cancer occurred amongst those workers with ≥20 years of exposure and mortality was excessive for those with ≥15 years exposure; the highest instances of lung cancer were observed following a latency period of 25-29 years (Koskela *et al.*, 1987).

Systemic Effects of Silica Exposure

Silicosis has also been associated with scleroderma, renal abnormalities, hepatic abnormalities, rheumatoid pneumoconiosis, systemic lupus erythematosus, rheumatoid arthritis and susceptibility to bacterial infection, which may be the result of immune function changes associated with silica exposure (Calvert *et al.*, 2003, Green & Vallyathan, 1996). Silica has an adjuvant effect on the production of antibodies, that is a non-specific

enhancement of immune response to an antigen (Parks *et al.*, 1999). This effect is not well-understood, however, it appears to be linked to the inflammatory response; one theory is that the activation of macrophages at the site of silica deposition leads to increased antigen processing and accelerated antibody production (Parks *et al.*, 1999). The cellular mechanism implicated in the development of auto-immune disease following crystalline silica exposure remains unknown (Calvert *et al.*, 2003) and results of studies have been mixed (Cooper *et al.*, 2002). A review of silica exposure noted that four occupational cohort studies found a threefold increased risk for the development of scleroderma, whilst five population-based control studies yielded mixed results (Cooper *et al.*, 2002). For rheumatoid arthritis, five occupational cohort studies found a fivefold (or higher) increase, and for lupus a >10-fold increase was determined in three occupational cohort studies (Cooper *et al.*, 2002). For ANCA-vasiculits (anti-neutrophil cytoplasmic autoantibody), a disease where small blood vessels are destroyed by inflammation (Kumar & Clark, 2009), a fourfold increase was observed in three case-control studies (Cooper *et al.*, 2002).

2.4 Volcanic Ash and Human Health

Ash from magmatic eruptions (defined as pyroclasts ≤2mm) forms when expanding gases cause magma to fragment as it decompresses (Heiken & Wohletz, 1985). Ash from phreatic (interacting with water) eruptions is created when magma chills as it interacts with water (either ground or surface water) which results in violent eruptions (Heiken, 1974, Heiken & Wohletz, 1985). Ash also forms through enhanced comminution, either in pyroclastic density currents (PDCs, also known as pyroclastic flows) (e.g., 1980 Mt St. Helens, 1995 – present Soufrière Hills, Montserrat eruptions) or in the conduit following explosive fragmentation (e.g., 1992 Mt. Spurr eruptions) (Rose & Durant, 2009). Explosive eruptions, especially phreatomagmatic, generate a higher proportion of fine ash in comparison to effusive eruptions (Horwell, 2007, Horwell *et al.*, 2010b). Following explosive fragmentation, collapse of the column results in the generation of PDCs in which blocks will be further fragmented. At dome forming volcanoes, collapse of pressurized lava domes, and associated PDC activity, generates ash which contains more

respirable material than most explosive eruptions (Horwell, 2007). This enrichment in respirable material is particularly due to preferential elutriation of the finest component of the flow into a lofting co-PDC plume (Horwell *et al.*, 2001). In magmatic eruptions, the morphology of larger ash particles is controlled by vesicle (cavity) density and shape (Heiken, 1974, Heiken & Wohletz, 1985). Respirable particles, however, tend to be uniformly blocky and angular apart from occasional fibre-like particles (Horwell, 2007, Horwell *et al.*, 2013a, Horwell *et al.*, 2010a, Horwell *et al.*, 2010b).

A variety of studies into the respiratory hazard of volcanic ash have been conducted, most notably since the eruption of Mt. St. Helens in 1980 (Bernstein *et al.*, 1986, Buist *et al.*, 1986, Merchant *et al.*, 1982). These can be broadly defined in three categories: epidemiological and clinical studies, in vivo and in vitro toxicology, and physicochemical characterisation. The most in-depth studies have focussed on three major eruptions, Mt St Helens (USA), Soufrière Hills (Montserrat) and Sakurajima (Japan). The former two eruptions are of significant interest due to their comparatively high crystalline silica content (Baxter *et al.*, 1999, Merchant *et al.*, 1982) and the latter two eruptions are long-duration events (Hillman *et al.*, 2012, Horwell *et al.*, 2014).

2.4.1 Epidemiological and clinical studies

Over 30 epidemiological and clinical studies have been conducted in the wake of volcanic eruptions, mainly focussing on the three aforementioned eruptions. These studies variably involve medical questionnaires, interrogation of hospital records and health surveys of populations (incorporating radiographic studies and lung function tests). The majority of these studies have addressed the acute symptoms associated with ash exposure, primarily due to the difficulties involved with following populations over the necessary timescale (decades) required for symptoms of chronic disease to become apparent. Following the eruption of Mt. St. Helens, an increase in hospital admissions for asthma and bronchitis was observed amongst those communities who had experienced the heaviest ashfall (Baxter *et al.*, 1981). In the week before the eruption there were 92 ER (emergency room) visits and 42 admissions, in the week following the May 18th eruption there were 301 ER visits and 92 admissions (Baxter *et al.*, 1981).

On Montserrat, a study of school children was conducted in 1998, nearly three years into the eruption of the Soufrière Hills volcano (Forbes *et al.*, 2003). This survey included asthma diagnoses, respiratory symptoms, exercise-induced bronchoconstriction and a review of individuals' current and previous exposure to volcanic ash. The results revealed symptoms of wheezing amongst children who had been exposed to ash in the past year (18% in ≤12 years old, 16% in >13 years old); with those exposed to greater amounts experiencing more severe symptoms. The results of exercise-induced bronchoconstriction in the 8–12 year old age group, was four times greater for children who had been heavily exposed to ash when compared to those children exposed to low ash levels (Forbes *et al.*, 2003). A more recent study (carried out in 2007) revealed that there was no longer any effect on asthma discernible amongst school children and no signs of volcanic ash health effects were evident in the chest X-rays of the most exposed children (Baxter *et al.*, 2014). No other comparable studies on long-term eruptions have been conducted.

A study of hospital records following the June 1996 eruption of Mt. Ruapehu, New Zealand was carried out in the cities of Auckland, Hamilton (where fine ash was detected) and Wellington (control population) (Newnham *et al.*, 2010). The study revealed an increase in respiratory mortality: the number of respiratory-related deaths was higher in the month following the eruption than any other month that decade. The study took into consideration other influential factors (urban air pollution, adverse weather conditions and influenza), however, the mortality signal of volcanic ash persisted with Hamilton (closer to the eruption) being more severely affected than the more distal Auckland (Newnham *et al.*, 2010).

The sole study which systematically tested for chronic disease development followed loggers in the wake of the Mt. St. Helens eruption who, due to their moderate ash exposure, developed acute respiratory symptoms within six weeks of the main eruption (Merchant *et al.*, 1982). They did not however, display any differences in lung function and their acute symptoms dissipated after a six month period. The duration of the exposure to ash from Mt St Helens, however, was not long enough to sufficiently

investigate the potential chronic effects (Merchant *et al.*, 1982). The eruption at the Soufrière Hills volcano has been on-going for over 15 years, however the population is too dynamic (emigration of those highly exposed soon after eruption commenced and immigration of workers in recent years to assist in re-building) for a large scale epidemiological study of chronic effects. A full meta-analysis of epidemiological and clinical studies is provided by Horwell and Baxter (2006).

2.4.2 Toxicology

Around 60 toxicological studies have been carried out on volcanic ash, again conducted chiefly upon the products of Mt. St Helens, the Soufrière Hills and Sakurajima. The focus of these has been crystalline silica toxicity, with cristobalite being the key polymorph of health concern. Due to the compositional heterogeneity of volcanic ash, it has not been possible to isolate volcanic cristobalite for toxicological analyses so measurements have been carried out on bulk or respirable (separated) samples. Results have been highly variable, mainly as a consequence of variation in study design, and have mostly shown the ash to be fairly inert; at the Soufrière Hills volcano it has been concluded that the ash is of a similar toxicity to coal mine dust (fairly inert (Borm & Tran, 2002, Stone *et al.*, 2004)) despite its high crystalline silica content (up to 23 wt. % (Horwell *et al.*, 2014)). A few *in vivo* studies at Mt. St Helens did, however, find fibrosis (Horwell & Baxter, 2006) but in these cases the animals were exposed to unrealistic doses of ash, although they were exposed over long durations to better mimic the effects of chronic exposures. Haemolysis is a generic toxicity test which measures erythrocyte (red blood cell) rupturing in the presence of the test substance (i.e. ash). These experiments have historically indicated a haemolytic potential (damage to erythrocyte membranes) in some volcanic ash samples (Vallyathan *et al.*, 1983). These analyses, however, were conducted on ovine erythrocytes and as the experiments were carried out days after the cells were collected they were naturally more fragile (Jikuya *et al.*, 1998, Parpart *et al.*, 1947). Modern haemolysis experiments on similar ash samples have utilised freshly collected human erythrocytes, which have yielded different results, with little haemolytic activity observed (Damby *et al.*, 2012). Recently, *in vitro* work with alveolar epithelial (lung) cells has shown a chronic pro-inflammatory response from volcanic ash from both the Soufrière

Hills, which is rich in cristobalite, and from the Icelandic Eyjafjallajökull and Grímsvötn volcanoes which are cristobalite-free; this indicates that silica is not the cause of the observed reactivity (Horwell *et al.*, 2013a). This range of responses from differing cell types highlights the complexity of determining the toxicity pathways involved; toxicological benchmarking currently requires further development via a greater range of bio-reactive assays conducted on volcanic ash of varying magmatic composition and eruption type (Horwell *et al.*, 2013a).

2.4.3 Physicochemical Characterisation

Physicochemical characterisation of volcanic ash is carried out for three reasons: 1) for fundamental research to determine why volcanic ash may/may not be toxic; 2) to accompany toxicological studies to define the structural side of the 'structure-toxicity' relationship; 3) for rapid assessment of health hazard during volcanic crises, when it is impractical to embark on epidemiological, clinical or time-consuming toxicological studies.

In terms of fundamental research, recent work has been carried out to determine why cristobalite-rich volcanic ash appears less reactive than one would expect for crystalline silica-rich dusts (Horwell *et al.*, 2012). A study into the nature and formation of volcanic cristobalite in lava domes revealed that volcanic cristobalite is impure, with up to 3 wt. % Al_2O_3 substituted into the silicon tetrahedral sites; furthermore, during the break up of lava domes, cristobalite crystals are often coated in adhered phases (such as glass and feldspar), which are also aluminium-rich, from the surrounding groundmass (Horwell *et al.*, 2012). Experimental studies have shown that the reactivity of quartz can be dampened by coating the crystal surfaces with aluminium lactate (Duffin *et al.*, 2001).

Volcanic cristobalite occurs as prismatic and platy crystals deposited from a vapour phase and as a groundmass phase resulting from devitrification in volcanic domes (Damby, 2012, Horwell *et al.*, 2013b); a study of ash from the recent explosive eruption of Chaitén volcano has also revealed the presence of cristobalite nano-fibres in the <4µm fraction as fibre aggregates (Reich *et al.*, 2009). Reich et al. (2009) propose that

cristobalite nano-fibres form in the eruption column in the presence of reducing agents (such as CO_2), which differs from the in-situ crystallisation of vapour phase and devitrification cristobalite in dome rock (Baxter *et al.*, 1999, Horwell *et al.*, 2013b). This raises new concerns regarding the potential toxicity of crystalline silica in this form due to its morphological similarity to asbestos. It is important to note, however, that this is the only documented occurrence of crystalline silica in this form and more commonly fibres in volcanic ejecta are comprised of minerals innocuous to health, such as gypsum (Bargar *et al.*, 1995, Horwell *et al.*, 2010a).

In recent years, several rapid assessments of health hazard have been carried out following a protocol developed by Horwell et al. (2010) for the International Volcanic Health Hazard Network, which involves physicochemical and toxicological analyses of ash (Damby *et al.*, 2012, Horwell *et al.*, 2013a, Horwell *et al.*, 2010a, Le Blond *et al.*, 2010). The protocol has been applied during several eruption crises (Damby *et al.*, 2012, Horwell *et al.*, 2013a, Horwell *et al.*, 2010a, Le Blond *et al.*, 2010), with the author contributing to two published studies which are presented in Appendix V. Many of the analytical techniques were developed or modified specifically for volcanic ash studies (Horwell, 2007, Horwell *et al.*, 2007, Le Blond *et al.*, 2009) and have been utilised in this project.

2.5 Fate of Inhaled Particulate

2.5.1 Particle-Lung Interaction: Particle Deposition

Deposition of particles within the lungs occurs when particles come into contact with the epithelium (cells which line the lung) of the nasopharynx or tracheobronchial tree, or with the alveoli (Cotes & Steele, 1987). Particle deposition can occur by impaction, sedimentation (due to gravity), diffusion (Brownian motion) resulting from the particles being impacted by adjacent gas molecules, interception and electrostatic deposition (Cotes & Steele, 1987, McClellan, 2000). These mechanisms are illustrated in Figure 2.2. These deposition mechanisms are strongly influenced by particle size and shape (McClellan, 2000, Seaton, 1999) as is summarised in Table 2.4.

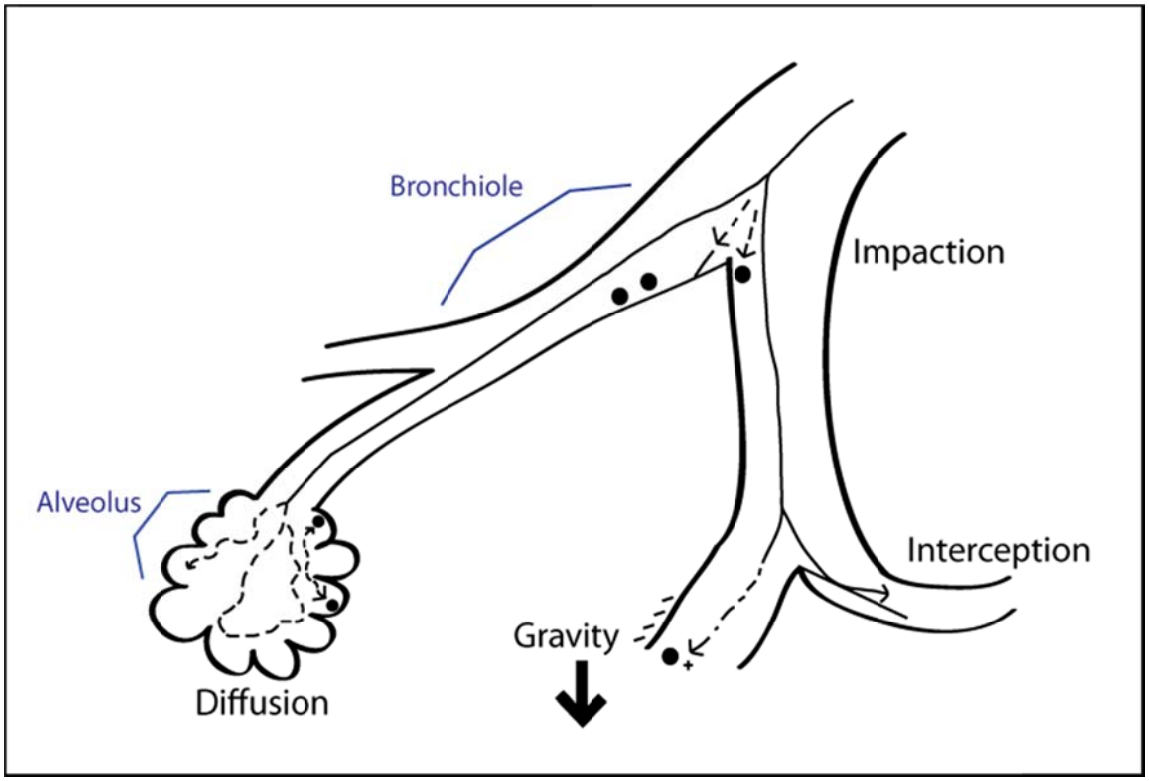

Figure 2.2 The mechanisms of particle deposition in different parts of the lung. After McClellan, 2000 (McClellan, 2000).

Table 2.4 Deposition of particles and fibres from respired gas. After Cotes and Steel, 1987 (Cotes & Steele, 1987). *Particles and most fibres which deposit in the airways are cleared via the mucociliary escalator. § For mouth breathing, with nose breathing the clearance rate is greater but alveolar deposition is reduced by ~25%.

Aerodynamic diameter	Principal Mechanism	Main Site*	Clearance (%)
> 20 µm	Sedimentation	General atmosphere	100
20 – 7 µm	Impaction	Nose, oropharynx (behind tongue), carina (main bronchi)	100
7 – 5 µm	Impaction, interception (fibres)	Nose, carina, bronchial bifurcation (split)	80
5 – 0.5 µm	Sedimentation	Alveoli, bronchioles	50§
0.5 – 0.05 µm	Diffusion	Alveoli	25
0.05 – 0.01 µm	Diffusion	Alveoli, bronchioles, bronchi	40

2.5.2 Particle-Lung Interaction: Particle Clearance

The clearance of particles deposited in the respiratory system occurs via various mechanisms depending on their location (and by implication, the particle size) and is variably effective (Table 2.2). In the nasopharyngeal tract, mucus containing trapped particles is removed through sneezing, blowing or may flow into the pharynx where it will be swallowed. In the trachea, particulatesare cleared partially by coughing and partially by the movement of cilia. Ciliated cells line the trachea, bronchi and bronchioles (Cotes & Steele, 1987, McClellan, 2000, Plumlee & Ziegler, 2003). Co-ordinated beating of the cilia transports mucus laden with particulates up the respiratory tract, where it is either coughed up or swallowed (known as the mucociliary escalator) (Plumlee & Ziegler, 2003, Seaton, 1999). Alveolar macrophages are mobile defence cells whose tasks include the ingestion of foreign bodies, secretion of defensive chemicals and recruitment of other macrophage cells. Within the alveolar region and bronchioles, clearance of particles takes place through dissolution in the fluid which lines the alveoli or via phagocytosis (ingestion) by alveolar macrophage cells. Phagocytosed particles, as well as some free particles may be cleared by the mucociliary escalator upward through the airways, into interstitial lung spaces, or through the alveolar membrane into the lymph or circulatory systems (Cotes & Steele, 1987, Plumlee & Ziegler, 2003, Seaton, 1999).

Macrophages contain lysosomes (intracellular organelles containing hydrolytic enzymes) with acidic pH and digestive enzymes designed to dissolve inhaled particles. Whilst this defence system is designed to deal with foreign bodies which the macrophage engulfs, the cell contents are potentially toxic to the body itself in the event that ingested material damages the macrophage and the intracellular enzymes and oxidants are released locally (Cotes & Steele, 1987, Cotran *et al.*, 1998, Seaton, 1999). The chemical composition of the particles along with their surface area and lung burden (how many particles the lungs are trying to clear) determines their rate of dissolution and clearance; the greater the ratio of surface area to particle mass (i.e. the smaller the particles) the more rapid the rate of dissolution, however, some chemical compositions do not dissolve easily (McClellan, 2000, Oberdorster *et al.*, 1992). It has been long established that particles of silica rapidly kill macrophages whereas other particles of comparable size and surface area (e.g. carbon black or diamond dust) are phagocytosed (ingested) by the cells

without harmful effects upon the macrophage (Allison *et al.*, 1966). For example, Allison et al. (1966) conducted comparative analyses on macrophages which revealed that cells which had phagocytosed silica started to suffer the toxic effects rapidly, whilst those which had phagocytosed diamond dust remained healthy for at least 30 hours (Allison *et al.*, 1966). This suggests that the lysosomal membrane plays a significant role in determining whether an ingested particle is toxic and is supported by observations that silica interacts with proteins, phospholipids and biological membranes (Allison *et al.*, 1966). The solubility of silica as the cause for this biopersistence (time that an intact particle remains in the lung) was suggested as far back as 1947, however, the exact nature of the interaction still remains unresolved (King, 1947). The biopersistence of crystalline silica in the lung is of interest to this study because some volcanic settings have been shown to produce material with appreciable quantities of crystalline silica (Baxter *et al.*, 1999, Baxter *et al.*, 1983, Horwell *et al.*, 2010a) which may generate silica-rich dusts when they are quarried.

A study on rat lungs by Hemenway et al. (1990) which followed short-term exposures to two different types of quartz and one type of cristobalite at three different concentrations, revealed that the amount of cristobalite cleared from the lung was considerably less than that of the two quartz materials, with little or no clearance after the initial 30 days post exposure (Hemenway *et al.*, 1990). A more recent study by Zhang et al. (2002) on the relationship between silica and apoptosis (programmed cell-death, usually as part of tissue regulation) revealed that the neutrophil (a type of white blood cell) and not the alveolar macrophage is the primary inflammatory cell which suffers apoptosis in response to particles of silica in rat lungs. Exposure to a low toxicity control (TiO_2) also produced transient pulmonary inflammation at high doses but was associated with a low level of apoptosis (Zhang *et al.*, 2002).

2.5.3 Particle-Lung Interaction: Oxidative Stress Response

Oxidative stress is an imbalance resulting from an excess of pro-oxidants compared with anti-oxidants in the body (Sies, 1991). The biological significance of this process lies in the reactivity of the molecules involved; free radicals (atoms with unpaired electrons produced through crystal cleavage during fragmentation, see Section 2.6.4) are potentially dangerous as they can react indiscriminately with neighbouring molecules, resulting in the oxidation of lipids, proteins and nucleic acids, leading to their loss of function (Kelly & Mudway, 2007). In the case of quartz, free radicals can arise from the particle surface (as described in Section 2.6.4) and they can also be formed following the recruitment of inflammatory leukocytes to the lungs. Studies indicate that activated oxygen species from the quartz-induced inflammatory cells are capable of causing mutations in the epithelial cells of the lung which can be a precursor to epithelial lung cancer (Clouter *et al.*, 2001). As discussed in Sections 2.6.3-2.6.4, below, a second mechanism for volcanic ash toxicity (in addition to silica) may be iron-catalysed hydroxyl radical generation, which has the potential to catalyse DNA, lipids and proteins, thereby instigating lung diseases (Hardy & Aust, 1995).

2.6 Factors Controlling Particle Toxicity

A number of factors affect the potential of dust to be toxic to the respiratory system; the principal factors are: morphology (size and shape), composition (both bulk and surface), surface area, solubility, and exposure (quantity of dust inhaled). The theory behind these factors is described here as these are the principal characteristics investigated in this study.

2.6.1 Particle Size

The shape and size of inhaled particles determine both the depth to which particles can penetrate the lung and the extent to which they can be cleared.

The largest inhaled particles are deposited in the mucous linings of the nasopharyngeal tract (Plumlee & Ziegler, 2003). The exact size of these particles is not definitively constrained, however they are roughly >10-100µm in aerodynamic (assumed spherical) diameter (Harrison *et al.*, 1996, Plumlee & Ziegler, 2003). The <100µm size fraction is termed the inhalable fraction and can penetrate the nose and throat. Progressively smaller sized particles can penetrate deeper into the lungs. Particles with a size of ≤10µm are termed the thoracic fraction and can penetrate the upper lungs, where they can become trapped in a layer of mucus lining the airways (Harrison *et al.*, 1996, Plumlee & Ziegler, 2003). Particles which can reach the alveoli (where gaseous exchange takes place) are known as the respirable fraction and are <4 µm (Beckett, 2000b, Horwell & Baxter, 2006). These finest particles are either trapped in the alveoli or are exhaled (Plumlee & Ziegler, 2003). The depth to which particles penetrate the lungs has an effect upon which types of disease can potentially be instigated; the thoracic fraction is implicated in acute diseases and the respirable fraction in chronic diseases. The relationship between particle size, depth of lung penetration and disease, is shown in Figure 2.3 and has been used to develop conventions for measuring occupational exposure. These conventions (shown in Figure 2.4) provide target specifications for the design of health-related sampling instruments which operate with a 50 % efficiency (where at least 50 % of the material will be less than, or equal to, the cut-off size). Nano-scale particulates, do not behave in the same way as the respirable fraction (their activity is akin to proteins) and they are beyond the scope of this thesis.

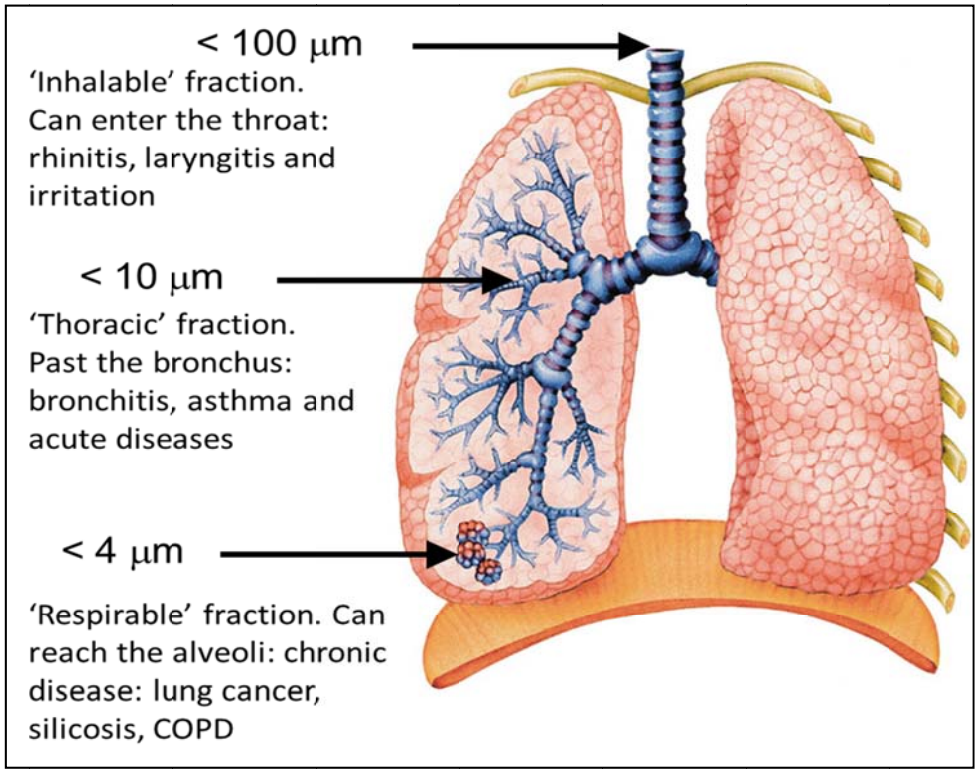

Figure 2.3 Diagram illustrating particle size, depth of penetration within lungs and associated diseases. Image courtesy of K. Donaldson, with text from presentations by C. Horwell (2009).

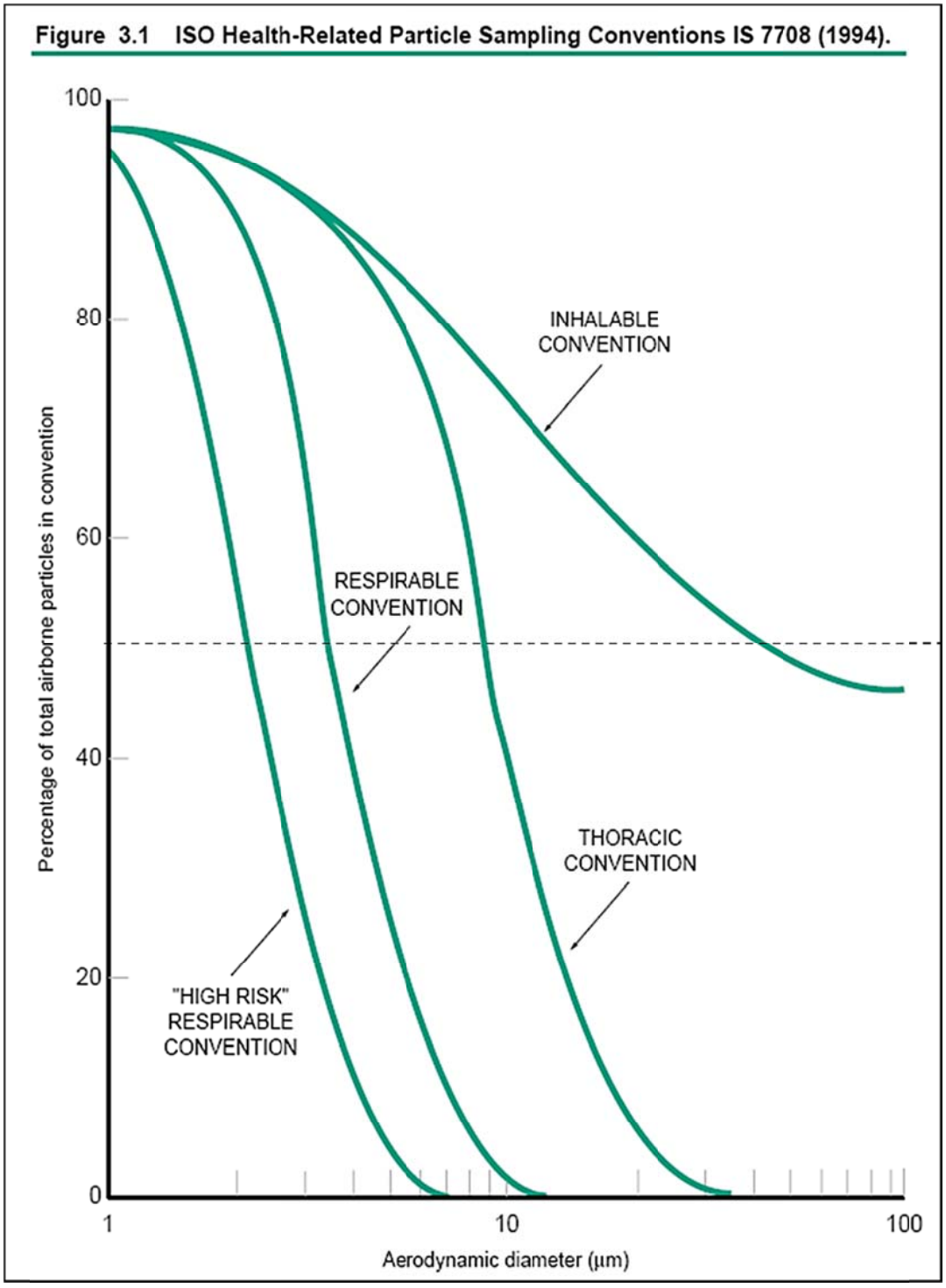

Figure 2.4 The health-related particle sampling conventions as employed in occupational exposure surveillance (Harrison *et al.*, 1996). They are based on 50% efficiency, where 50% of the material will be less than or equal to the cut-off size.

2.6.2 Particle Shape

The shape of particles is an important factor in the determination of particle toxicity because certain morphologies, such as fibres, are difficult for the lung to clear due to their high aspect ratio (Seaton, 1999). The World Health Organisation (WHO) has defined the morphology of (asbestiform) fibres in occupational settings: fibres over 5 μm in length with an aspect ratio >3:1 and a diameter of less than 3μm. Their length and thinness means they are easily inhaled as they line up with the direction of airflow; upon exhalation, however, airflow is more turbulent and subsequent turning against their long axis in the smaller airways causes them to impact (Kumar & Clark, 2009). Studies of asbestos toxicity reveal several factors are responsible for fibre pathogenicity: length, diameter, durability and surface properties, and concentration (Seaton, 1999). The shape of volcanic ash can vary depending on the type of magma and style of eruption (Heiken, 1974, Heiken & Wohletz, 1985). The presence of fine, acicular glass shards in volcanic ash (such as in the explosive eruption of Mt. St. Helens (Baxter *et al.*, 1983)) is not considered to be health significant (Horwell & Baxter, 2006).

2.6.3 Particle Composition

The composition of natural mineral particles is significant because some minerals or mineral groupings can elicit a toxic response in the lungs (Berube *et al.*, 2004, Donaldson & Borm, 1998, Jones & Berube, 2007, Nash *et al.*, 1966, Vallyathan *et al.*, 1992). Around a third of the continental crust is made up of silicon dioxide, most of which takes the form of the polymorph quartz (with cristobalite and tridymite also present in smaller quantities) (Jones & Berube, 2007). In 1997 the International Agency for Research into Cancer classified crystalline silica as a Group 1 human carcinogen (a 'promotion' from group 2), based on evidence of carcinogenicity in experimental animals and in humans (IARC., 1997). The evaluation of evidence noted, however, that carcinogenicity to humans was not detected in all industrial settings and that several studies on quartz alone have yielded variable results, indicating that the hazard posed by quartz is controlled by the origin of the sample or the presence of other chemicals or minerals within its structure (Donaldson & Borm, 1998). Quartz is the most common polymorph of crystalline silica,

however, in some volcanic domes, cristobalite can be found (Horwell *et al.*, 2014, Horwell *et al.*, 2010a, Horwell *et al.*, 2013b). Some volcanic settings are also conducive to the formation of the polymorph tridymite; both tridymite and cristobalite are meta-stable at ambient temperatures (Damby, 2012). Quarrying of volcanic rocks which contain these polymorphs can expose workers to dust containing crystalline silica, which is of most respiratory concern when it is freshly fractured (Jones & Berube, 2007).

In terms of other volcanic minerals with toxic potential, very little research has been conducted to define these. Research has focussed on iron-rich minerals (e.g. amphiboles, pyroxenes, pyrite and oxides) as these are capable of producing the deleterious hydroxyl radical (Horwell *et al.*, 2003). Minerals such as feldspar are not thought to be reactive (Berube *et al.*, 2004) and neither is amorphous volcanic glass, because of its solubility (Fubini *et al.*, 2001, Napierska *et al.*, 2012, Warheit, 2001).

2.6.4 Surface Composition

The surface composition of a particle may not be the same as the bulk composition, which is significant because it is the particle's surface that will be the site of any interaction with the lung, assuming the particle is insoluble. The surface of ash is subject to processes (such as leaching and weathering, see Section 2.6.5) which can lead to differing compositions to the bulk (Ayris & Delmelle, 2012). Furthermore, collision between ash particles (such as during comminution, for example) may form new (post eruptive) surfaces, which may also have different composition to the bulk ash (Ayris & Delmelle, 2012); this is of particular interest to quarrying, where processing material involves grinding which will similarly give rise to new, fresh surfaces. The generation of mineral dusts with fresh surfaces (e.g. quarry extraction, erupted ash) can potentially create radicals as fragmentation may cause cleavage of the atoms, resulting in loss of electrons (Horwell *et al.*, 2007, Horwell *et al.*, 2003).

Radicals are highly reactive as they attempt to complete their electron pairing (Flaschka, 1969). Surface radicals on fresh silica surfaces form as the silicon-oxygen bond is cut; homolytic cleavage results in dangling bonds (two radicals) and heterolytic

cleavage creates surface charges (a cation and an anion). This is significant for quarrying where dust with fresh surfaces may be generated following extraction or processing of material. Such dust may potentially be more toxic than quarry dust that has been exposed to weathering, for example, in the stockpiles of processed material. However, Horwell et al. (2003) found no evidence of silica surface radicals on cristobalite-rich Soufrière Hills volcanic ash.

In addition to alteration of surfaces due to weathering, particle surfaces may actually have a different mineralogical composition to the bulk particle. For volcanic ash, it is known that groundmass glass and microlite phases often adhere to the surface of cristobalite crystals, thereby occluding the silica from the lung environment (Horwell *et al.*, 2012). This silica occlusion principle has been observed in other dusts too, such as in low rank coal dusts where crystalline silica may be coated in clay (Stone *et al.*, 2004). It is these external factors (in addition to the inherently variable characteristics of the different silica polymorphs) which make prediction of silica toxicity so challenging (Donaldson & Borm, 1998).

2.6.5 Solubility and Leaching

Volcanic ash which has been lofted in a plume may have volatiles adsorbed onto its surfaces. If these volatiles are soluble they may be leached from the ash surface, for example by rain in the environment, or by fluids in the lung (Taunton *et al.*, 2010, Witham *et al.*, 2005). Such leaching (or weathering) can also remove elements from the ash particle itself (not just those adsorbed from the plume) with common examples including Mg, Ca, Na and K (Witham *et al.*, 2005). It is important to note, however, that some adsorbants from the plume can react with the particle surface thereby becoming much harder to remove by leaching. Those elements of chief health-concern include As, Ce, F, Fe, Hg, Pb, S (as the compound SO_4) and Se (Witham *et al.*, 2005). The addition of fluoride (from volcanic ash) to the environment can instigate the disease fluorosis amongst livestock (especially grazing animals), with over 1,000 ewes dying following the 1995 eruption of Ruapehu volcano, New Zealand (Cronin *et al.*, 2003) and most of Iceland's livestock following the 1783-84 eruption of Laki (Fridriksson, 1983). As there is no active

plume involvement during the quarrying process and the deposits are often weathered prior to material extraction, the leachate studies typically carried out upon volcanic ash samples are of less direct relevance to this study.

A study on the dissolution of rock-forming minerals in simulated lung fluid revealed that chrysotile had the shortest dissolution rate, followed (in order) by anorthite, potassium-feldspar and talc; with muscovite, kaolinite, albite and quartz taking the longest (no appreciable dissolution over 50 years) (Taunton *et al.*, 2010). During weathering, basaltic and interstitial rhyolitic glasses and olivine have been found to be the first phases which become altered relative to other crystalline phases (Gislason & Oelkers, 2003). Furthermore, basaltic glass weathering can be additionally enhanced by high surface areas (Gislason & Oelkers, 2003).

2.6.6 Surface Area

Surface reactivity experiments have shown that specific surface area is an important parameter in particle toxicity, particularly with regard to the extent of resultant cellular inflammation (Duffin *et al.*, 2002, Duffin *et al.*, 2007). There is also a very strong relationship with particle dosing Duffin et al. (2002) conducted in vivo experiments on rats, instilling a dust suspension into their lungs (Duffin *et al.*, 2002). The inflammation resulting from low-toxicity dusts did not appear to be related to the mass-dose (µg/ml) of particles instilled, however, when the dose was expressed as surface area (cm^2), a clear dose-dependent relationship was observed (Duffin *et al.*, 2002). This highlights the importance of exploring the surface area of quarried particulates and where possible adjusting surface reactivity experiments and toxicology tests by surface area.

2.6.7 Particle Concentration

Particle concentration within the lungs (or, lung dosimetry), is controlled by the deposition, clearance, retention, translocation and dissolution of inhaled particles; these are important factors governing the concentration and persistence of particles in the lung and therefore their potential to instigate pulmonary damage (Oberdorster *et al.*, 1994). A

key factor in particle toxicology is the Exposure-Dose-Response paradigm, which highlights the importance of differentiating the amount of dust inhaled, deposited and retained (Kreyling *et al.*, 2007). Dose is defined as the amount of particles retained after deposition and clearance as illustrated below by Oberdorster et al. (1994).

$$Retention = Deposition - Clearance$$

It is important to note that biopersistance mechanisms can vary in different parts of the lung with ultrafine particles eliciting a consistently high inflammatory reaction (Oberdorster *et al.*, 1994). Whilst the inhaled dose is usually given as particle mass, other expressions may be more applicable depending upon the mechanisms of the response produced, for example particle volume, surface area (see 2.5.7 above), or particle number.

2.7 Exposure and Risk Perception

A study of the global burden of non-malignant respiratory diseases arising from occupational airborne exposures concluded that they are an important cause of death and disability worldwide (Driscoll *et al.*, 2005). Most of these cases can be prevented by implementing improved health and safety approaches, principally through improved engineering and working conditions (Driscoll *et al.*, 2005). The reduction of silica dust exposure levels which has occurred during the last century in the developed world has led to significant decrease in morbidity and mortality from both silicosis and silica dust associated tuberculosis (Hnizdo & Vallyathan, 2003). Despite this, however, chronic obstructive pulmonary disease (COPD) continues to pose a health risk to silica-exposed workers (Hnizdo & Vallyathan, 2003), as does silicosis and TB in developing nations.

2.7.1 Exposure

The exposure of quarry workers to potentially toxic dusts is governed by two principal factors; the first is the concentration of respirable dust and the second is protective measures taken to reduce dust inhalation. The concentration of respirable dust will depend upon a variety of factors including: the weather, the size of the operation, the

mode of extraction, the rock type and the type of processing (whether it involves crushing and water). Whether a worker takes steps to protect themselves is mainly controlled by local regulations (either set by the country, legislative area or quarry company) but may also be a personal decision in areas where legislation is lax or respiratory protection is not mandatory. In this case, the decision may depend on the worker's perception as to whether the dust constitutes a risk to their health. Risk perception is a complex area due to the multiplicity of influences that shape attitudes, awareness, insights and beliefs (Blong, 1984). The reluctance to participate in hazard mitigation strategies cannot be simply determined as resulting from a lack of knowledge but may be due to other life pressures (Barclay *et al.*, 2008). Understanding how workers perceive risk is therefore fundamentally important for improving risk communication and reduction (Haynes *et al.*, 2008b). Exposure legislation and factors which affect exposure (weather, climate, economy, quarry vehicles etc.) are discussed in *Chapter 6* - The Exposure Hazard of Volcanic Quarry Dust and Associated Risk Management.

2.7.2 Risk Perception

Perception of hazards in relation to quarrying has focused upon the effects of quarrying on the surrounding environment, especially with regard to local residents (Bloodworth *et al.*, 2009, Kaliampakos & Menegaki, 2010, Major & Vardy, 1989), even the perceptions of disused quarries as tourist sites have been considered (Edwards & Cotes, 1996). Fewer investigations have explored issues of quarry worker perception in relation to occupational hazard (Bajpayee *et al.*, 2004) and the author was unable to find any in relation to perception of dust hazard specifically. There are, however, synergies between occupational medicine, public health and disasters (Morgan *et al.*, 2008), with numerous associated risk perception studies (Barclay *et al.*, 2008, Haynes *et al.*, 2008a, Haynes *et al.*, 2008b). A growing body of evidence concerning perception in natural hazards has emerged in recent decades, including perception of, and communication regarding, volcanic hazards (Barclay *et al.*, 2008, Haynes *et al.*, 2008a, Haynes *et al.*, 2008b).

Assessing perception and communication lies mainly within the realm of social science, the language of which differs markedly to that of the physical sciences. Defining

terms such as 'risk' is often complex (even within disciplines), however, without conceptual clarity, miscommunication and confusion are likely to occur whether dealing with subjective, qualitative approaches or quantitative procedures (Fischhoff *et al.*, 1984). To bring greater clarity to this interdisciplinary research, some key concepts are defined here. A *hazard* can be described as an event which poses a threat to people or their property (McGuire *et al.*, 2002) and has varying degrees of intensity or severity (Wisner *et al.*, 2004b). Environmental hazards can be categorised in a variety of ways, one example is as natural (extreme geophysical and biological events), technological (major accidents) or contextual (global environmental change) (Smith, 2004).

UNESCO (United Nations Educational, Scientific and Cultural Organization) have defined *risk* as the possibility of a 'loss' (of life, of property, of productive capacity etc.) (UNESCO, 1971), however, risk is currently perceived as a compound function of hazard and vulnerability where vulnerability also incorporates a 'value' (number of lives at stake, capital value etc.) by hazard managers, insurance agencies and academics (Fournier d'Albe, 1979, Wisner *et al.*, 2004a). *Vulnerability* itselfis being prone or susceptible to damage or injury; it is the characteristics of a person or group which influences their "capacity to anticipate, cope with, resist and recover" from the effects experienced following a hazard event or process (Wisner *et al.*, 2004b). Risk is often as a function of the hazard multiplied by vulnerability (Wisner *et al.*, 2004b).

Vulnerability in hazards has a temporal dimension, that is, vulnerability is not limited to the event itself but can lead to further impacts in the future. There are also variables which can influence vulnerability including occupation, gender, health status and age (Wisner *et al.*, 2004b), which are all relevant to the quarrying industry.

Risk perception and risk assessment vary greatly. The latter is usually carried out by trained experts and eliminates emotive features in order to produce replicable results (Smith, 2004). Risk perception, however does not have a replicable outcome because it presents itself differently to different people, with all responses weighted equally valid and every individual selecting their personal response (Smith, 2004). It is likely that risk perception varies between quarry managers (who receive information from regulatory bodies) and their employees (who receive instructions regarding dust mitigation from

their managers); therefore, it is important to evaluate the perception of workers as this will inform their own response with regard to quarry dust exposure.

2.8 Conclusion

Despite a long-standing knowledge of the connection between crystalline silica exposure and the morbidity and mortality of quarry workers, many tens of thousands of people globally remain occupationally exposed to such dusts. The mechanisms involved in silica toxicity, and indeed in the toxicity of many other minerals, are not yet fully understood and epidemiological outcomes not fully constrained. Whereas many studies have been conducted on siliceous rocks and mixed siliceous dusts (coals, sandstones, granites etc.) the specific hazards posed by deposits of extrusive volcanic origin have received little detailed study. It is thought that two main factors control the potential toxicity of volcanic ash (free radical generation and crystalline silica content) and it is important to determine whether volcanic quarry dusts can pose an analogous hazard.

The findings of epidemiological and exposure studies raise concerns about the effectiveness of any existing mitigation strategies for reducing dust exposure. Whilst exposure studies encompass measurements of ambient air concentration and clinical studies assess lung function, little work is being done to measure the effectiveness of hazard communication in a quarry and to test whether the effectiveness of mitigation strategies may be linked to the understanding of workers in respect of the hazard posed. This project aims to assess the hazard of volcanic quarrying on the basis of known parameters of volcanic ash toxicity (incorporating both mineral and toxicological characterisation) and to appraise these in the context of management and risk perception at the sites investigated. Details of the quarries selected are presented in the following chapter, *Chapter 3 - Geological Setting of the Study Sites.*

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Chapter 3 – Study Sites and their Geological Setting

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3.1 Introduction

The quarrying of volcanic products is a global activity, with all types of deposit being quarried to provide material for a variety of uses and applications. This chapter gives the geological background to each of the quarry sites included in this study and provides an overview of operations at quarries extracting mafic, intermediate and felsic material.

Mafic and intermediate lavas are often used in construction and for road building. Figures for the usage of these specific rocks are hard to obtain because non-volcanic rocks can also be used for construction and road aggregate purposes. Felsic deposits such as pumice, pumicite (finer-grained pumice) and perlite are sold for very specific uses and some statistics are presented in Table 2.2 (Chapter 2).

Perlite is an alteration product which is formed when dacitic or rhyolitic glass becomes hydrated. This usually occurs as a result of interaction with fluids or gases, which create a network of cracks around a core of unbroken glass (Denton *et al.*, 2009). On Yali (Greece) perlite has formed as a result of phreatomagmatic activity, when rising hot lava met sea water (Hatzilazaridou, 2002). Perlite is rich in water (2-6 %) and when it is heated rapidly (to 871^{o}C) it expands 4-20 times its original volume as the water vaporizes to create a large volume of vesicles, and, hence, a very low density material (Bayansaikhan *et al.*, 2007).

The variety of volcanic products quarried gives rise to the variation in potential hazard; it is therefore important that a broad range of quarried volcanic material is investigated. To this end, eleven volcanic quarry field sites were studied, along with several samples of non-volcanic material as comparisons and controls.

The quarries investigated range from mafic to felsic and incorporate one volcanically active site. The sites were located in New Zealand, Montserrat and Greece and their individual geological settings are described in Section 3.2. New Zealand was selected because quarrying is a major industry and a wide range of volcanic products are commercially utilised; notably, basaltic lava flows and rhyolitic pumice, ash and obsidian. Montserrat was chosen on the basis that the quarried deposits were of a different magmatic composition and deposit type to those sampled in New Zealand; namely, intermediate ancient and modern pyroclastic density currents, which are known to contain crystalline silica (Baxter *et al.*, 1999). Montserrat also had the advantage that it is volcanically active and thereby poses a unique opportunity to sample an area where both

occupational and environmental exposure occurs. Whilst there were some felsic quarries in New Zealand, the global economic downturn had led to a decline in sales of felsic material (notably pumice); this meant that no new extraction or processing was taking place. To provide a full spectrum of investigation into magma and deposit types, the Greek island of Yali was chosen as the final field site, where active extraction and processing of both pumice and perlite took place.

3.2 Quarry Locations and their Geological Setting

Half of the quarries sampled were located in the North Island of New Zealand, forming part of the Auckland Volcanic Field (AVF), the South Auckland Volcanic Field (SAVF), the Taupo Volcanic Zone (TVZ), and the Tangihua Ophiolite Complex (TOC). Field work was carried out in early spring of 2009, for six weeks. The quarries visited were primarily of basaltic (AVF and SAVF and TOC) and dacitic-rhyolitic (TVZ) origin. On Montserrat, andesitic material is quarried at three locations and fieldwork was carried out over a four week period in early 2010. Additional rhyolitic material was sourced from Greece, a major international producer of pumice and perlite; the sites chosen were two quarries on the islet of Yali and fieldwork was conducted over a 5 day period during the summer of 2010.

3.2.1 The Auckland Area

Quarries in this area were chosen on the basis that they had active extraction (drilling and blasting of lava flows) and processing taking place, that they represented different eruptions, and that they were owned by different companies and therefore may have differing processes and corporate dust-management strategies. Two quarries owned by the multinational Winstone Aggregates were chosen: Puketutu Island in the AVF and Hunua as a non-volcanic comparison in the Hunua ranges. Bombay quarry, owned by the multinational Holcim was selected from the SAVF. These locations are shown in Figure 3.1.

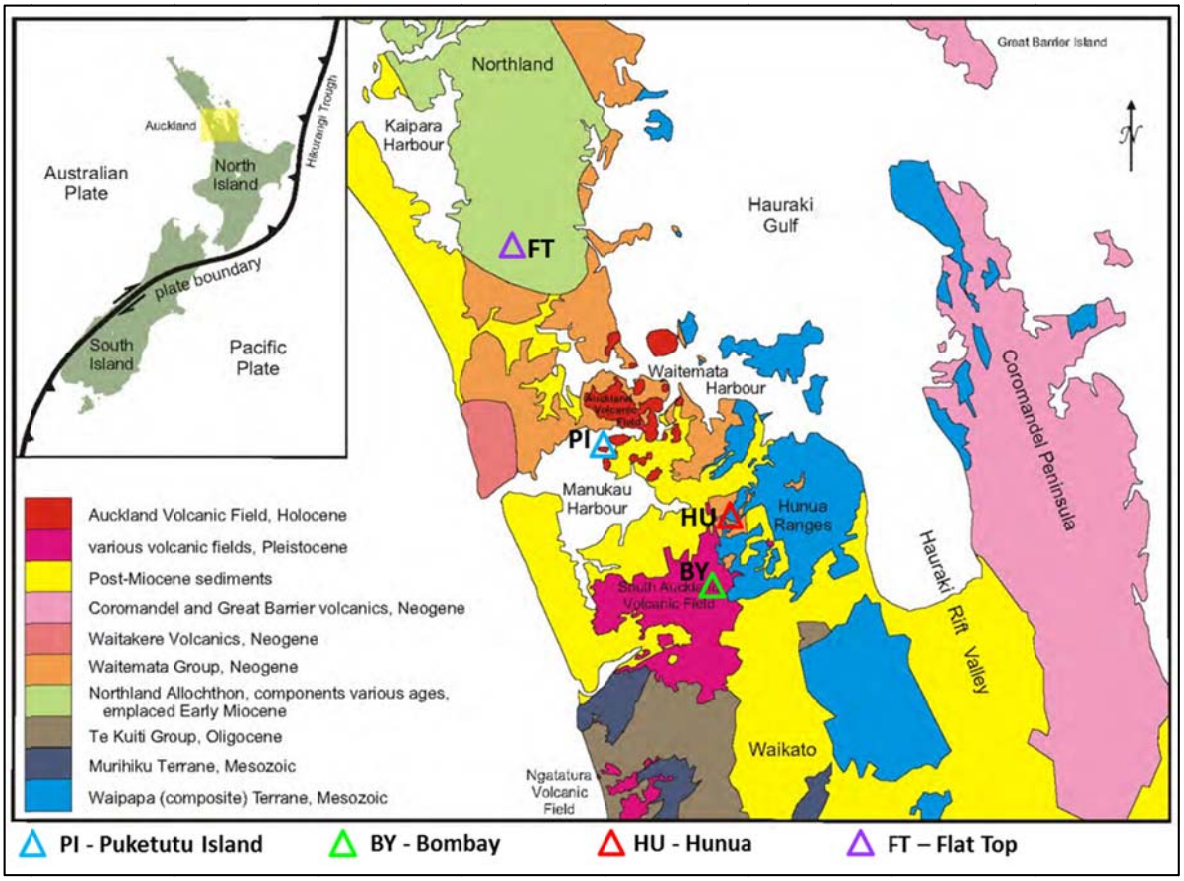

Figure 3.1 Simplified geological map of the Auckland region, North Island, New Zealand. Inset: Plate boundary through New Zealand. After Kenny et al. (2011).

The AVF overlies a magmatic hotspot approximately 100 km beneath the city of Auckland and comprises 49 monogenetic volcanoes most of which are cones <150 m high (Smith & Allen, 1993). The erupted magma is basaltic and the oldest eruptions occurred over 100,000 years ago. The last eruption occurred 600 years ago, so the area is still considered to be active (Smith & Allen, 1993). The mineralogy of the AVF is characterised by olivine-rich alkali basalt and basanites, with a typical composition including: olivine, clinopyroxene and feldspar, with minor apatite and Fe-Ti oxides (Smith *et al.*, 2009). The island of Puketutu, located in the AVF, has been privately owned since 1845 and quarrying began in 1964; parts of the quarry are now being in-filled with biosolids as part of its restoration and it will re-open to the public as a regional park over a 35-year period (McGee Lucy, 2012, Watercare, 2012). Figure 3.2 shows the deposit being quarried at Puketutu Island.

The SAVF is composed of 97 monogenetic volcanic centres within an area of 300 km^2. The products are basaltic and range in age from 0.51 to 1.59 Ma (Briggs *et al.*, 1994).

Bombay quarry, shown in Figure 3.3, lies in the SAVF, it was established in 1997 and produces ~700,000 tonnes of quarry material annually (Holcim, 2011).

Figure 3.2 Processing the basaltic flows at Puketutu Island quarry, North Island, New Zealand.

Figure 3.3 The basaltic lava flow deposit at Bombay quarry, North Island, New Zealand.Inset: scoria.

The Hunua Ranges is an area of clastic rocks, with faces containing thin lenses of spilite, chert, and volcanic argillite. Pillow lavas are separated from the underlying greywackes and are in contact with a thick sequence of chert (Sporli, 1978). The greywackes

(immature sandstone with >15% clay (Keary, 2001)) are of Permian age and are being quarried at Hunua quarry (Sporli, 1978). Small-scale quarrying of the greywackes began at Hunua in the 1920s; the current operation by Winstone Aggregates began in 1956 and is one of the largest operations in North Island, shown in Figure 3.4 (Winstone Aggregates, 2012). The methods of material extraction (by blasting) and processing (crushing and screening) are similar to those at the mafic quarries in the area, which made it a suitable comparison.

Figure 3.4 Greywacke quarrying at Hunua quarry, North Island, New Zealand.

3.2.2 The Taupo Volcanic Zone

The supervolcano Taupo is considered one of the most frequently active and productive rhyolite calderas in the world. It is now partly filled by Lake Taupo underlain by a magma chamber at a depth between 6 and 8 km below the lake (Froggatt, 1993). The first eruptive activity began over 65ka BP and since then a random pattern of exceptionally large events have occurred interspersed by smaller eruptions. The eruptive behaviour is typical of all the major rhyolite volcanoes of the central North Island and, together, they have produced large eruptions about every 50,000 years (Froggatt, 1993, Houghton *et al.*, 1995). Rhyolite accounts for ~ 98% of all erupted material in the TVZ, but there are also small amounts of dacite and basalt (Froggatt, 1993). Most of the rhyolite has been erupted explosively as pumice and ash that has been spread widely over the Taupo area

(Froggatt, 1993). Figure 3.5 shows the locations of the Taupo Volcanic Zone and of the three rhyolitic quarries studied.

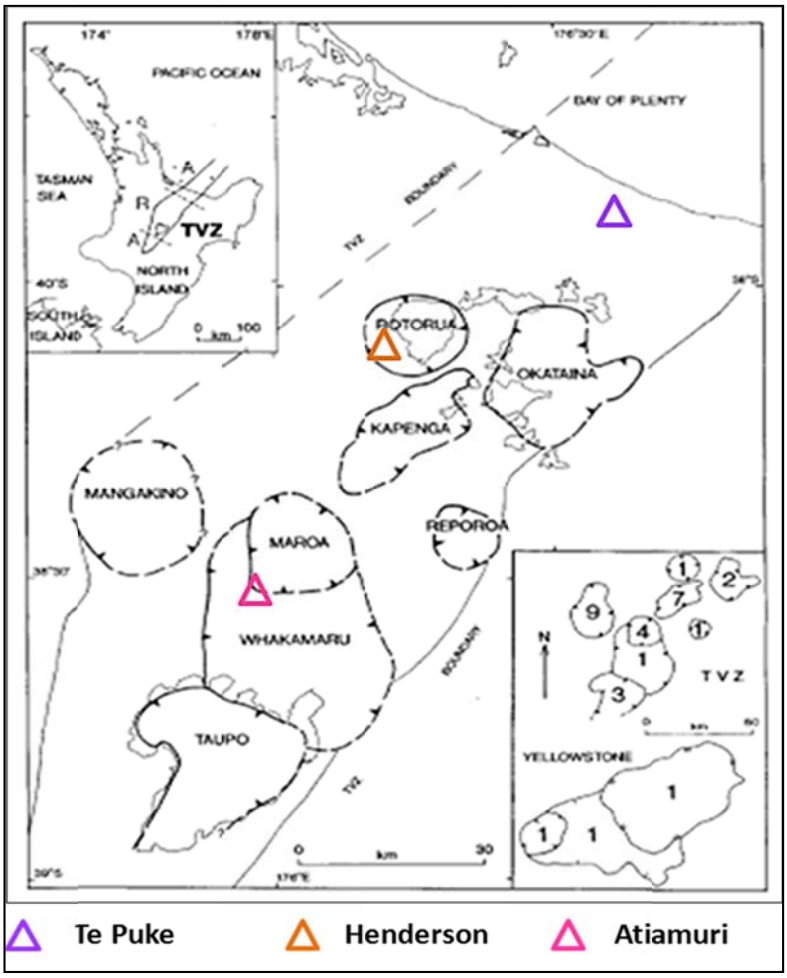

Figure 3.5 Map of the Taupo Volcanic Zone (TVZ). The top inset shows the position of TVZ on the North Island of New Zealand and division of the zone into segments dominated by andesite-dacite (A) and rhyolite (R) volcanism. The bottom inset shows comparative maps of Taupo and Yellowstone calderas (numbers are caldera-forming events). After Houghton et al, (1995).

Little extraction and processing was taking place at the quarries, mainly as a result of difficulties in selling stockpiled processed material since the start of the global financial downturn in autumn 2008. The sites were chosen for their variation in deposits (airfall pumice and ash, which will have differing grain sizes) and because some purchasing was taking place and therefore further extraction and processing was expected in the near future.

Te Puke is a rhyolitic pumice quarry with material originating from the Okatania centre, including air fall pumice and ash deposits, ash layers include the Okareka ash erupted 18 ka BP (Nairn, 1992). It is owned by the multinational Winstone Aggregates. A section of the quarry, showing the layers of air fall material is shown in Figure 3.6.

Figure 3.6 The quarry wall being excavated at Te Puke quarry (part of the Okatania volcanic centre in the TVZ) showing layers of ash and pumice air fall deposits.

Atiamuri Sand and Pumice is an independent company operating as a subsidiary of Inpro. The quarry extracts pumice (Figure 3.7) from the Whakamaru volcanic centre within the TVZ and process 40,000m^3 of material per annum.

Figure 3.7 The quarry wall, with large pumice deposits, being excavated at Atiamuri, part of the Whakamaru volcanic centre, TVZ, North Island, New Zealand (biro to indicate scale).

Henderson's quarry (Figure 3.8) extracts obsidian from the Ngongotaha dome, which forms part of the Rotorua volcanic centre in the TVZ (Dadd, 1992). This independent quarry was not visited as part of the field campaign, however, four samples of dust from

this quarry were sent by F. Von Aulock of Liverpool University (UK) for a MSci project by J. Close (Close, 2012), the results of which are incorporated within this thesis.

Figure 3.8 Henderson's quarry, Ngongotaha dome, TVZ, North Island, New Zealand.

3.2.3 The Tangihua Ophiolite Complex

The Flat Top quarry is operated by Winstone Aggregates and lies in the TOC, to the north of the Auckland Volcanic Field, shown in Figure 3.1 (Black, 2012). It is comprised of massive basaltic lava pillow sequences, combined with intercalated sediments and lesser gabbro, microgabbro and basaltic intrusions (Nicholson *et al.*, 2000). Recent research by Whattam et al. (2004) suggests the deposit formed 26-29 million years ago in a supra-subduction zone (indicating rapid extension of fore-arc oceanic crust during the initiation of the subduction). Although their age is not well established, they are the oldest of the mafic deposits studied in this thesis. They are comprised predominantly of microcrystalline basalts with phenocrysts of plagioclase and clino- and ortho- pyroxene; and, less commonly, olivine and hornblende. Secondary phases include chlorite, smectite and illite clays (Nicholson *et al.*, 2000). Flat Top quarry excavates the massive pillow lava sequence, shown in Figure 3.9.

Figure 3.9 Flat Top quarry, quarrying pillow lava from the Northland Allochthon, North Island, New Zealand.

3.2.4 The Aegean Back-Arc

The islet of Yali forms part of a back-arc of volcanic islands in the Aegean Sea within the Mediterranean basin (Figure 3.10). The area is characterised by intermediate to deep focused seismicity, consistent with active subduction (Keller, 1982). From the stratigraphic record and radiometric dating volcanism in the Aegean arc began during the Pleiocene and reached a peak in activity during the Quaternary (Keller, 1982). Nysiros island is considered to be active, with strong fumarolic activity and phreatic eruptions until the end of the 19th century; the neighbouring islet of Yali has experienced several prehistoric pumice eruptions. Yali is exclusively rhyolitic, the north-eastern part being characterised by obsidian domes and perlite, whilst the south-western part is comprised of air-fall pumice deposits. The obsidian domes have been dated at 24ka BP (fission track), however, pumice beds formed by the most recent eruptions overlie collections of primitive pottery and Neolithic obsidian artefacts, demonstrating that the most recent volcanic activity is younger than the Neolithic in age (Keller, 1982).

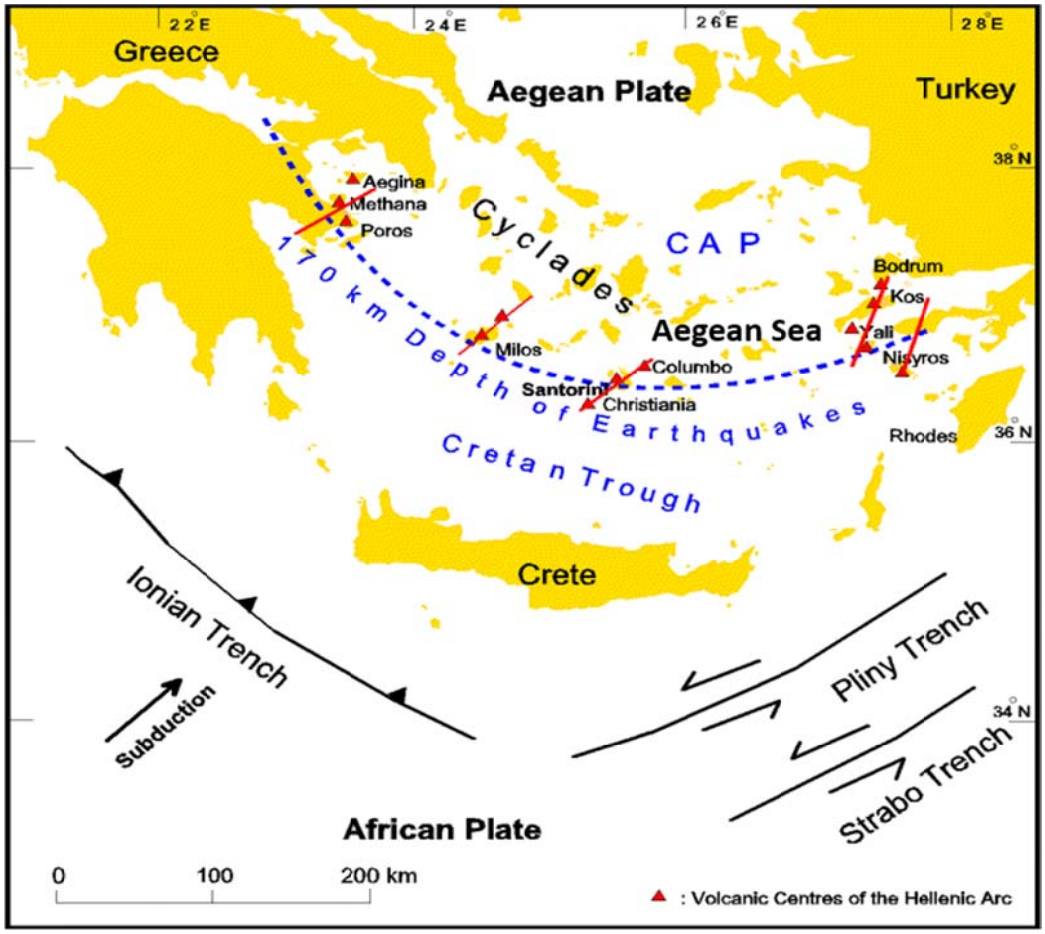

Figure 3.10 The Aegean back arc with location of Yali indicated in the eastern Aegean. After Geophysics Online: National and Kapodistrian University of Athens(Louis, 2012).

There are two quarries on the islet of Yali. LAVA quarries the pumice deposit and is owned by the multinational Lafarge, while a smaller company Aegean Perlite quarries the perlite deposit. Both were studied but with the majority of work being undertaken at the larger pumice operation. Their locations are given in Figure 3.11 and the deposits illustrated in Figures 3.12 and 3.13. Unexpanded perlite was collected directly. Expanded perlite was also sourced from British Gypsum, in order to determine the respiratory hazard of this form of processing, which was not carried out on the island.

Figure 3.11 Yali, part of the Aegean back-arc.

Figure 3.12 The pumice deposit at LAVA quarry, Yali islet, Greece.

Figure 3.13 The perlite deposit at Aegean Perlite quarry, Yali islet, Greece. Top inset: an area of quarry wall with outer layer removed, to ensure sampling is of material with a fresher surface (scale in cm). Bottom inset: a section of the obsidian dome

3.2.5 Montserrat

The island of Montserrat is situated in the northern part of the Lesser Antilles volcanic island arc, which formed as a result of the westward subduction of the Atlantic oceanic lithosphere beneath the Caribbean plate (Kokelaar, 2002). The island is made up chiefly of porphyritic andesites with sporadic basaltic outcrops (Young *et al.*, 1998).The Soufrière Hills volcano in the south of the island is predominantly andesitic and the current eruption began in 1995 commencing with a phreatic phase (Kokelaar, 2002). On-going eruptive activity has been characterised by a wide variety of phenomena including: growth of andesitic lava domes, generation of pyroclastic density currents (PDCs), by lava dome collapse and by fountain collapse in explosive eruptions, Vulcanian and sub-Plinian explosivity with accompanying tephra fall, sector collapse (and associated debris avalanche and high-velocity PDCs) and the generation of lahars (Sparks & Young, 2002).

Three quarries were visited on Montserrat. Their locations are shown in Figure 3.14, along with the ages of the deposits as determined by $^{40}Ar/^{39}Ar$ dating. The quarries are at Little Bay, in the north of the island, where old Silver Hills dome deposits are quarried, Trants where PDC deposits are quarried from the current eruption and the Belham Valley where PDC material deposited by lahars is quarried from the current eruption (Figure 3.15). The Soufrière Hills lava is andesitic, coarse-grained, porphyritic and crystal-rich (Murphy *et al.*, 2000). The Silver Hills is composed primarily of two-pyroxene andesite lava and loose pyroclastic deposits (Rea, 1974) and is shown in Figure 3.16.

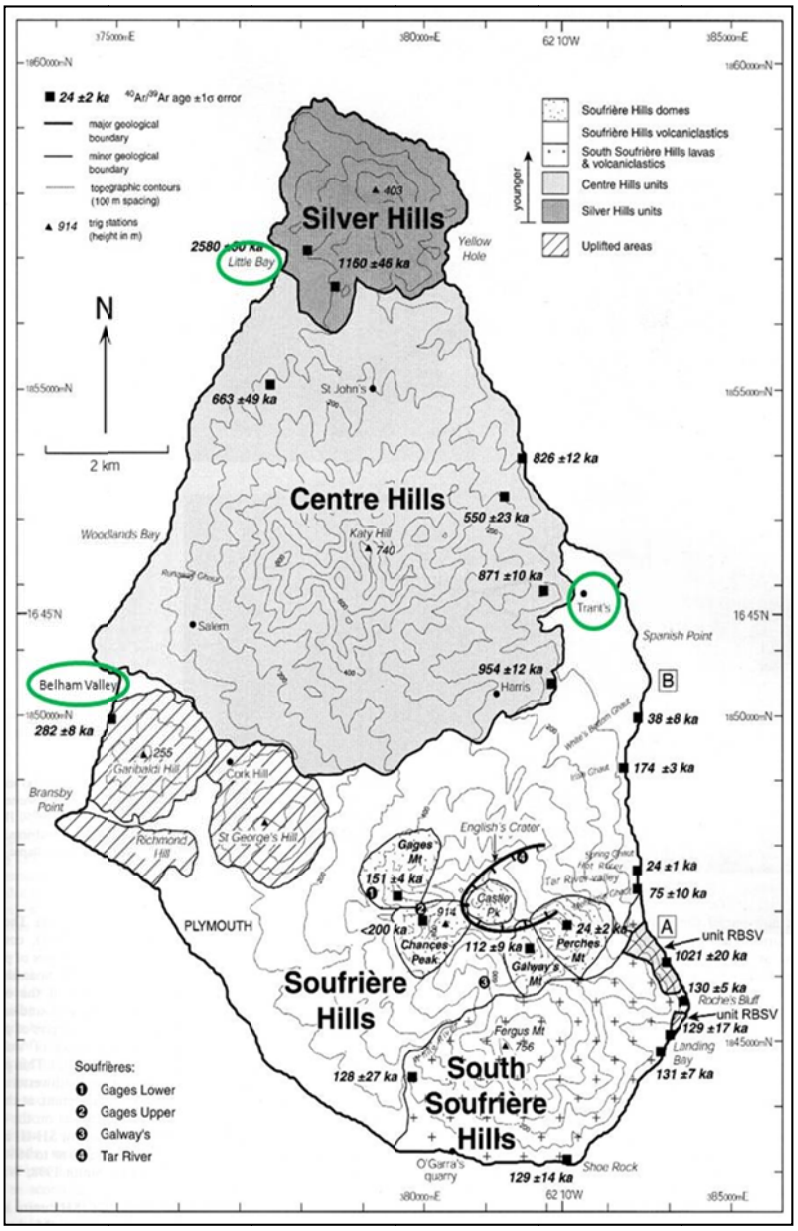

Figure 3.14 The island of Montserrat and the three quarry locations. After Harford et al., (2002).

Figure 3.15 The Belham Valley, Montserrat, West Indies. Inset: a pit created by a digger removing material.

Figure 3.16 The Little Bay quarry, Montserrat, West Indies.

3.2.6 Moneystone

Two samples of sandstone were provided for this study from Moneystone quarry (Staffordshire). The quarry extracts sandstone from Carboniferous Millstone Grit, which is very rich in quartz. The raw material is processed by crushing and screening, applying methods similar to those used at the mafic quarries in New Zealand. However, the material is also leached with acid to remove minerals except quartz and heat treated, during which it becomes transformed into cristobalite. The cristobalite sand is then sold for commercial applications; however, the quarry was closed shortly after samples were collected, due to the economic recession, and therefore no monitoring of airborne dust could be undertaken.

The key geological features of the quarries visited are summarised in Table 3.1. Further details of their operations, including number of workers, type of processing, sizes of finished product are provided in Appendix I.

Table 3.1 Geological setting and deposit type at the quarries studied. *Magma type determined by X-ray fluorescence, detailed in Chapter 4.

Country	Geological Area	Quarry Name (sample code)	Magma or Rock Type*	Deposit Type
New Zealand	Auckland Volcanic Field	Puketutu Island (P2)	Tephrite/Basanite	Lava
	South Auckland Volcanic Field	Bombay (BY)	Trachybasalt	Lava
	Hunua Ranges	Hunua (HU)	Greywacke	Clastic rocks
	Taupo Volcanic Zone	Atiamuri (AT)	Dacite	Pumicite
		Te Puke (TP)	Rhyolite	Pumice
		Hendersons (HE)	Rhyolite	Obsidian dome lava
	TangihuaOphiolite Complex	Flat Top (FT)	Basalt to Basaltic Trachy-Andesite	Lava
Greece	Aegean Back-Arc	Lava (LA)	Rhyolite	Pumice
		Aegean Perlite (AP)	Rhyolite	Perlite
Montserrat	Silver Hills	Little Bay (PH, LB)	Andesite	Ancient pyroclastic density currents
	Soufrière Hills	Trants (ED, BF, JN)	Andesite	Recent pyroclastic density currents
		Belham Valley	Andesite	Lahar deposits
UK	Staffordshire Moorlands	Moneystone	Sandstone	Millstone grit

3.3 The Quarrying Process

The processes of extraction, processing and distribution were broadly similar at operations quarrying material from comparable types of deposit. For example, all solid rock deposits (e.g. basaltic lava flows and greywacke) were extracted through drilling and blasting, whereas friable deposits are extracted by using a digger. The processing of raw material into different sizes of finished product involved crushing and screening (sieving) which could either be done wet or dry (water is used to prevent dust from silting up the screens). Harder rocks (such as those from massive lava flows) required more crushing than friable deposits to achieve the desired size. The finished product was typically stored as stockpiles at all sites, but its movement off-site varied significantly depending upon whether it was removed by trucks or ships. The following section illustrates the progression of quarrying, from extraction, via processing to finished product, for the mafic, intermediate and felsic magma groups.

3.3.1 Quarrying Mafic Deposits

The processing of quarried material is illustrated in Figure 3.17. Rock walls are blasted and boulders are loaded onto dumper trucks by excavators. The boulders are taken to the processor where they are crushed and screened by size; the smaller the size of finished product required, the greater the number of crushers employed (typically cone or rotary crushers). The finished product is then transported by dumper truck and stockpiled ready for collection or delivery.

The process of drilling in mafic quarries (and the greywacke at Hunua) and accompanying blasting are illustrated in Appendix II. Samples of drilled, blasted and finished product were collected from these quarries.

Figure 3.17 The processing of raw material into finished product. Quarry shown is Bombay quarry, South Auckland Volcanic Field, New Zealand.

3.3.2 Quarrying Intermediate Deposits

The quarrying of intermediate deposits was investigated on Montserrat, where activity was significantly curtailed due to an extension of the volcanic exclusion zone. Material from Trants would usually be extracted by diggers and processed locally with crushing and screening, before being transported to a stockpile holding area in Little Bay. Similar extraction and processing typically takes place at Little Bay and in the Belham Valley.

The increase in volcanic activity in winter 2009-2010 led to the exclusion zone being extended to encompass the Trants and Belham Valley sites. The quarry face at Little Bay where extraction had been occurring, was deemed potentially unstable and unsafe for further extraction. During the field season, therefore, all three quarries had stopped active processing, and so no samples of raw material could be obtained. However, samples could still be collected of dust accumulated on the processors from previous processing (Figure 3.18) and from the finished product. Entry to the quarry site in the Belham Valley, in the exclusion zone, was co-ordinated with the assistance of the Montserrat Volcano Observatory.

Figure 3.18 Dust accumulated on base of the girder of the processor at Little Bay, Montserrat, West Indies.

3.3.3 Quarrying Felsic Deposits

The active quarrying of felsic deposits was studied on Yali. Here, as for other friable deposits, raw material from the pumice quarry was extracted using a mechanical digger. Due to the friability of the quarry floor, trucks were not able to drive in the areas being quarried. The only vehicles on site were the diggers and front loaders, the latter moved extracted material to the tunnels, and both vehicle types have a weight-distributing caterpillar tread. Material was moved via a series of tunnels and conveyor belts (Figure 3.19) to the processor and to ships. Similar methods for extraction of took place at the perlite quarry but with material from the site of excavation transported to the processor by a front loader. Samples of raw and finished product were obtained as well as dust accumulated on the processor.

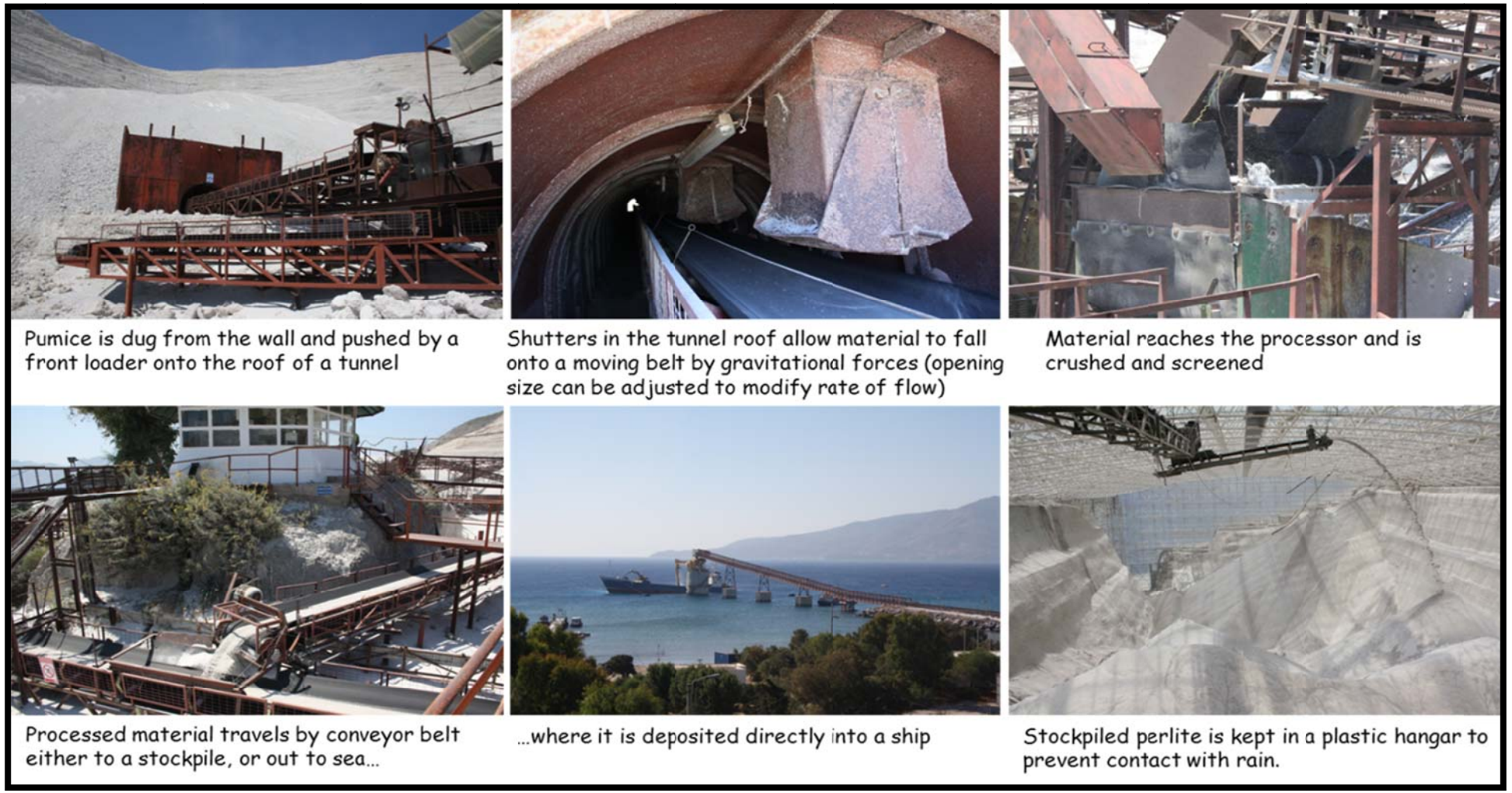

Figure 3.19 The process of quarrying felsic deposits on Yali, Aegean Sea.

3.4 Conclusion

Volcanic deposits quarried around the world range in composition and type from basaltic lava flows, through andesitic and rhyolitic ash and pumice, to rhyolitic obsidian and perlite. The quarrying is associated with a range of techniques for extraction and processing, depending on the nature of the deposits. Typically, solid rock deposits such as massive lava flows (e.g. the mafic quarries in New Zealand) and greywacke are drilled and blasted before being crushed. More friable deposits, such as the PDCs of Montserrat or pumice deposits (Yali and New Zealand) are excavated from the quarry wall with a digger and do not require drilling or blasting. All quarries produced a range of differently-sized finished product.

Different deposits and associated quarrying methods are likely to yield differences in dust hazard. The following chapters investigate the characteristics and toxicity of the different types of dust generated from: raw material extraction, processing and transportation, across the different quarries and aim to identify the potential airborne hazard posed at the locations studied.

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Chapter 4 – Physicochemical and Mineralogical Characteristics of Volcanic Quarry Dust

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4.1 Introduction

For all mineral dusts, the physicochemical characteristics of the dust will govern the toxicity of the particles once in the lung. These characteristics lie at the heart of understanding particle toxicity; however, as the majority of particle-based toxicity studies have focused primarily on elicited chemical and/or biological responses, the contribution of physicochemical parameters is less well understood (Donaldson & Borm, 1998, Donaldson *et al.*, 2007, Duffin *et al.*, 2002). As described in Chapter 2 (sections 2.6.3 and 2.6.4), crystalline silica displays variable toxicity (Donaldson & Borm, 1998) and physicochemical properties (as well as the condition of the surface) are postulated as possible reasons for this variability (Fubini, 1998b, Fubini *et al.*, 2001, Fubini *et al.*, 1995). In recent years, many studies have explored the physicochemical characteristics of volcanic ash alongside potential toxicity (Damby *et al.*, 2013, Horwell *et al.*, 2010b, Horwell *et al.*, 2012, Jones & BeruBe, 2011, Le Blond *et al.*, 2010) and those techniques are applied here to volcanic quarry dust.

The key physicochemical properties which control toxicity addressed in this chapter are: whole particle and surface composition, grain size, morphology and surface area. These physicochemical factors are outlined in Table 4.1, along with their particular relevance.

Table 4.1. Mineralogical factors governing potential pathogenicity of inhaled particulate. [§]Surface chemistry is discussed in chapter 5.

Mineralogical Factor	Health-relevant question addressed
Composition	Does it contain toxic elements or pathogenic minerals? Are those minerals occluded by more inert phases?
Grain Size	Can it be inhaled? Where does it deposit in the respiratory system?
Surface Area	If there is a reactive surface, how large is it?
Morphology	Can it be cleared from the lung? Where does it deposit in the respiratory system?
Surface Chemistry[§]	Are there reactive ions on the surface?

4.1.1 Composition

The composition of both volcanogenic quarry dust and volcanic ash is controlled by the magma type of the deposit and any post-depositional alteration. Knowledge of the major elements in the bulk composition can be used to determine the magma type, which can indicate the likely minerals present. The minerals of primary health concern in volcanic dust are the crystalline silica polymorphs - quartz, cristobalite and tridymite - due to their well-documented health effects (Chapter 2). Volcanic ash can contain significant quantities of quartz and cristobalite (e.g. up to 23 wt.% in some ash samples from Soufrière Hills Volcano (Horwell *et al.*, 2014)). Most mafic magmas contain <5% crystalline silica (Le Maitre, 1989) – with the exception of some tholeiitic basalt, due to silica oversaturation – however, intermediate and felsic magmas can drive eruptions where ash can contain substantial crystalline silica, >20 wt.% in dome collapse samples. In addition to crystalline silica, iron content is also a health concern (see Chapter 2); reactive iron on volcanic ash particle surfaces can originate from iron-bearing minerals such as olivine and pyroxene (Horwell *et al.*, 2003a), which are abundant in mafic magmas but more sparse in intermediate and felsic ones.

Determination of bulk composition is carried out here by XRF for major elements and classification through a total alkali silica (TAS) plot, this aids in determining that a range of magma types have been sampled as well as providing insight into their likely mineral assemblage. The crystalline silica content is semi-quantitatively determined through use of XRD with an internal attenuation standard and allows for comparison between samples from different magmatic types, modes of emplacement and different geographic locations.

4.1.2 Grain Size

Grain size can be regarded as the critical factor which governs health effects because particles must first be fine enough to penetrate into the lungs before other factors can influence any potential toxicity (Horwell, 2007). The size of a particle also influences the depth of penetration into the lungs and, consequently, the physiological response to the

dust. The relationship between grain size and depth of penetration is presented in Chapter 2 (Section 2.2.1) along with details of resulting diseases (Section 2.3.2).

A variety of volcanic quarrying processes can generate dusts and grain size analysis is conducted here by laser granulometry on different sample types to investigate whether they contain substantial inhalable material.

4.1.3 Specific Surface Area

The specific surface area of a dust particle is a critical parameter in the structure-toxicity relationship, by providing the required surfaces for toxicological interactions in the lung. Fine-grained dusts tend to have a greater average surface area than coarser material, despite making up a smaller mass or volume percentage of a dust sample. A basic paradigm in cellular toxicology is that:

$$Toxicity = specific\ surface\ area\ x\ specific\ surface\ reactivity\ x\ surface\ availibility$$

where specific surface reactivity is the reactivity per unit surface area (Donaldson *et al.*, 2007). The dependence on surface area is borne out in studies such as one by Duffin et al. (2002) which showed that inflammation was directly related to the surface area of various dusts instilled into rat lungs, irrespective of particle composition. The specific surface area of the quarry dust particles is determined here by nitrogen adsorption and the Brunauer, Emmett, Teller (BET) method (Brunauer *et al.*, 1938).

4.1.4 Morphology

The morphology of particles is important for particle deposition and clearance; for example, fibre-like particles can deposit deeper into the lung than spherical particles of equivalent mass and/or surface area due to their unique aerodynamic properties (Mauderly *et al.*, 2000), and may persist in the lungs due to inefficient phagocytosis of long, thin particles by macrophages (see Chapter 2, section 2.5.2).

In previous studies on the morphology of (non-volcanic) quarry dust, fibrous minerals have been identified, particularly in locations mining metamorphosed and

altered rocks (Bruni *et al.*, 2006, Burragato *et al.*, 2005, McDonald *et al.*, 2004). At aggregate quarries with non-fibrous deposits, typical morphologies consist of angular particles with sharp edges consistent with them being freshly formed in the crushing processes; well-rounded particles could be indicative of etching from rainwater dissolution, signifying that they have probably been in the environment for a longer time (Blades *et al.*, 2007). Previous analyses of the <2.5 µm fraction of quarry dust has shown that it is rare to find intact crystals in this fine size fraction (Jones *et al.*, 2003).

For volcanic ash, morphology is controlled by the type of magma and style of eruption (Heiken, 1974, Heiken & Wohletz, 1985). The respirable fraction usually exhibits a morphology which is uniformly blocky and angular, with occasional fibre-like particles (Horwell *et al.*, 2008, Reich *et al.*, 2009) and glass shards in explosive eruptions (Horwell & Baxter, 2006); these morphologies are comparable to the typically angular morphologies observed in quarry dust, although weathered particles tend to be well-rounded (Jones *et al.*, 2002, Ledda *et al.*, 2013).

The morphology of volcanic quarry dust and volcanic ash is investigated here using scanning electron microscopy (SEM) to observe the particle shapes and to quantify them through image analysis.

4.2 Aims and Hypotheses

The aim of this chapter is to investigate the physicochemical and mineralogical properties of volcanic quarry dusts, namely, their grain size, morphology, surface area and crystalline silica content, and to compare with both volcanic ash and non-volcanic quarry dusts. By comparing volcanic quarry dust with volcanic ash, it is possible to investigate whether ash could be used as a proxy for dust (or vice-versa) in relation to any of the parameters studied, thereby providing access to the wealth of literature on volcanic ash, which could aid in hazard assessment. The specific hypotheses are as follows:

1) *The proportion of thoracic (<10µm) and respirable (<4µm) material within volcanic quarry dust differs depending on which stage of the quarrying process it is produced at; e.g. raw material, processed, finished product.*

A key aspect of dust hazard assessment is the ability to discern whether certain quarrying activities or deposit types pose a greater hazard than others, for example, by generating

greater amounts of respirable material. This, in turn, allows hazard managers to plan mitigation measures accordingly.

The mode of fragmentation of quarried material is dependent on the deposit type, rather than magmatic composition, with solid deposits (e.g. lava flows or domes) requiring high-energy extraction (drilling, blasting and crushing), whilst friable deposits (such as scoria, pumice, volcanic ash and pyroclastic density current (PDC) deposits) require little energy for extraction and processing (Bohloli & Hoven, 2007, Guimaraes *et al.*, 2007). High-energy extraction typically generates finer material (Bohloli and Hoven, 2007); however, the grain size of the friable deposits is likely to vary from finer grained ash fall to coarser grained pumice, therefore it is important to appraise the quarrying process in conjunction with the specific deposit type.

2) *The proportion of thoracic (≤10µm) and respirable (≤4µm) material within volcanic quarry dust differs from that within erupted ash of the same magmatic composition.*

In this study, volcanic ash is being considered as a comparative benchmark for airborne hazard assessment; therefore, it is important to consider any potential differences in the respective proportions of respirable material.

The grain size of both volcanic quarry dust and volcanic ash is governed by the energy involved in fragmentation. The energy of eruptive explosivity is linked to magma type, with effusive basaltic eruptions tending to generate coarser ash than explosive silicic ones (Rose & Durant, 2009), whereas the grain size in quarries is controlled by the energy of different quarrying processes, as well as the deposit type.

3) *Volcanic quarry dust has a differing morphology to that of erupted ash.*

Certain morphologies, notably those with a high aspect ratio, behave differently in the respiratory system; therefore, morphology is an important parameter in assessing the hazard of occupational dust exposure. Volcanic quarry dust may differ in its morphology from ash due to the differences in their respective fragmentation processes, which may further impact upon the potential to use volcanic ash as a future benchmark in hazard assessment.

As outlined in Chapter 2, Section 2.5.2, the morphology of volcanic ash is determined by the magma type and eruption style (Heiken, 1974; Heiken and Wohletz, 1985); however, when quarrying solidified volcanic deposits, the industrial fragmentation mechanism may produce different dust morphologies to volcanic ash of the same magmatic composition. When comparing quarried friable material with volcanic ash, particles may have altered morphologies in comparison to their fresh counterparts if they have been weathered (Blades et al., 2007; Heiken, 1974).

4) *Volcanic quarry dust contains abundances of crystalline silica which are similar to volcanic ash from a comparable eruption type.*

Crystalline silica is a known carcinogen and determining whether erupted ash and volcanic quarry dust from the same source volcano (or comparable eruption setting) contain similar quantities of crystalline silica might allow for the use of volcanic ash as a benchmark in assessing this hazard parameter.

Studies of ash from certain volcanic settings reveal that some intermediate and felsic magmas can contain appreciable quantities of crystalline silica, particularly from dome-forming volcanoes (Damby, 2012, Horwell *et al.*, 2003a, Horwell *et al.*, 2010a). Here, quarry dusts derived from compositionally similar eruption settings are tested to determine whether they contain comparable quantities of crystalline silica. Furthermore, samples with comparatively high levels of crystalline silica are investigated to assess whether the silica presents as individual crystals or whether its surfaces are occluded by the presence of other phases; this has been observed on the surface of volcanic ash from the Soufrière Hills volcano (Horwell *et al.*, 2014) and can affect potential toxicity by providing a barrier between the silica crystal and the lung.

In order to address the above aims and hypotheses, a suite of physicochemical and mineralogical analyses were carried out. These include:

1. Grain size analysis, in order to quantify the amount of respirable material in each sample.
2. Crystalline silica quantification, in order to determine which samples contained significant amounts of cristobalite, quartz and/or tridymite.

3. Morphology analyses, to determine differences amongst the samples and styles of processing and also whether there are any fibre-like particles present.
4. Imaging of sectioned particles, in order to assess whether there are accompanying phases which might mask the toxicity of the crystalline silica.
5. Surface area analyses, to determine whether certain samples have higher available surfaces for lung reactivity.

4.3 Methodology

4.3.1 Sample Collection and Preparation

Samples were collected to represent the production cycle as widely as possible including raw material, dust produced by extraction or processing, and dust from stockpiles of finished product. The exact location within each quarry and type of samples collected varied depending on the individual quarry setup and deposit type, however, samples representing the full production cycle were obtained to ensure sample collection was systematic and comparable among quarries.

Samples were collected using a small plastic spatula and a plastic scoop, to avoid potential contamination from metal implements and with the aid of a natural fibre paint brush to minimize the loss of fines (Figure 4.1a). These implements were cleaned between the collection of individual samples. Where samples of raw material were collected from friable quarry faces, the outer layer of material was removed to expose a fresh surface for sample collection (Figure 4.1b).

Samples of volcanic ash were collected in the field in Montserrat into a pyrex glass dish; a paintbrush was used to eliminate the loss of fine dust when transferring to plastic sample bags. Further samples of volcanic ash were obtained from the collection of Claire Horwell (Durham University). Samples were selected to represent a range of magma types and eruption styles. As rhyolitic eruptions are comparatively rare, ash from only one felsic

eruption was selected. All ash samples used in this study were collected pristine (i.e. shortly after fallout and uncontaminated by rain).

Two types of non-volcanic quarry dust were selected as comparisons; a greywacke for the similarity in its quarrying process to that of mafic, solid lavas and a sandstone for its well-documented high crystalline silica content.

Figure 4.1 Sample collection in the field: a) using a natural fibre brush to minimise loss of fines during collection of blasted samples; b) removing the weathered outer layer from a perlite quarry face to collect samples of raw material.

The samples and collection details are presented in Tables 4.2 and 4.3.

Each bulk dust sample was placed into a Pyrex glass bowl and weighed prior to drying over night at 80^{o}C. The sample was weighed again after drying and then sieved manually for 60 sec. using Endecott stainless steel sieves through >2mm, 1-2mm and <1mm meshes to remove the non-ash-grade particles. Any particles adhered to the mesh were gently brushed off with paint brushes to minimize the loss of fines. Each of the fractions was then weighed, with the <1mm fraction used in most subsequent experiments.

OVERLEAF: Table 4.2 Quarried volcanic dust samples collected. Samples marked [§] are provided by Noel Worley of British Gypsum and * are samples collected by F. Von Aulock (Liverpool University).

Country	Magma Type	Deposit Type	Quarry	Collection Date	Details	Sample Name
New Zealand	Mafic	Lava (hard rock)	Bombay	21/02/09	Fines caught from drillers exhaust	BY_01
				04/03/09	Drilled fines	BY_02
				04/03/09	Post blast fines	BY_03
				04/03/09	Finished product (GAP 7)	BY_04
			Flat Top	10/03/09	Drilled fines	FT_01
				10/03/09	Post blast fines	FT_02
				10/03/09	Finished product: (GAP 25) finest product.	FT_03
			Puketutu	24/02/09	Drilled fines (fresh, drilled 23/02/09 or 24/02/09)	P2_01
				24/02/09	Finished product: (GAP 20) screened, blasted 5-6 months ago	P2_02
				24/02/09	Post blast particles, quarry floor.	P2_03
				11/03/09	Post blast fines, quarry floor.	P2_04
				11/03/09	Drilled fines (pre-blast)	P2_05
	Felsic	Pumice (friable, air fall)	Te Puke	19/02/09	Quarry floor, road behind digger wheel	TP_01
				19/02/09	Quarry Wall, freshly excavated face	TP_02
				19/02/09	Quarry floor, holding area	TP_03
				19/02/09	Finished product: (0-4 mm) screened.	TP_04
				19/02/09	Quarry Wall, ash layer	TP_05
				19/02/09	Quarry Wall, pumice layer	TP_06
				19/02/09	Finished product: finest grade (0-2mm)	TP_07
				19/02/09	Pumice piece quarry floor road	TP_08
			Atiamuri	30/03/09	Perlite from Tram Road near Atiamuri	AT_01
				30/03/09	Finished product: (1-4 mm) finest pumice product.	AT_02
				30/03/09	“cleanfill sand” <1.93 mm	AT_03
				30/03/09	Finished product: Pumicite (finer grained pumice)	AT_04
				30/03/09	Finished product: (4-10 mm)	AT_05
		Obsidian lava dome (hard rock)	Henderson	Summer 2011	Raw material	OBS_01*
				Summer 2011	Accumulated dust (on crusher)	OBS_02*
				Summer 2011	Accumulated dust (on crusher)	OBS_03*
				Summer 2011	Quarry floor	OBS_04*

Country	Magma Type	Volcano	Collection Date	Eruption Style	Sample Name
Nicaragua	Mafic	Cerro Negro	01/12/95	Strombolian-vulcanian eruption (1995)	CerNeg*
Italy		Etna	04/11/02	Strombolian eruption (2002)	Etna*
		Vesuvius	1872	Effusive strombolian eruption (1872)	V1872*
			1906	Violent strombolian eruption (1906)	V1906*
Guatemala		Fuego	29/10/74	Sub-plinian eruption (1974)	Fuego*
Iceland		Eyjafjallajökull	07/05/10	Effusive fissure eruption	Eyja_13*
Montserrat	Intermediate	Soufrière Hills	23/01/10	Ash venting eruption (2010)	MA_23
			28/01/10	Ash venting eruption (2010)	MA_28
			05/06/99	Dome collapse (1999)	Mon_99*
			12/07/03	Dome collapse (2003)	Mon_03*
Philippines		Pinatubo	04/07/91	Plinian eruption (1991)	Pina*
Chile	Felsic	Chaitén	02/05/08	Explosive eruption (2008)	Chai_02*
			02/05/08	Explosive eruption (2008)	Chai_05*

Country	Rock Type	Quarry	Collection Date	Sample Type	Sample Name
New Zealand	Greywacke	Hunua	06/03/09	Finished product: (PAP 5) finest grade.	HU_01
			09/03/09	Blasted fines	HU_02
			09/03/09	Drilled fines	HU_03
			09/03/09	Backbreak fracture (“Waitamata Ash”)	HU_04
Great Britain	Sandstone	Moneystone	09/11	Raw sandstone	MSR[§]
			09/11	Finished product	MSC[§]

Table 4.3 Comparative samples of volcanic ash and non-volcanic quarry dust used in this study. Samples marked * were obtained from the collection of Claire Horwell of Durham University. Samples marked [§] were provided by Paul Botham of Sibelco, from Moneystone quarry, UK.

Country	Magma Type	Deposit Type	Quarry	Collection Date	Details	Sample Name
Montserrat	Intermediate	Pyroclastic density current deposits (ancient)	Little Bay (Phoenix)	19/01/10	Dust from side of processor (origin: Little Bay)	PH_01
				19/01/10	Finest grade material (origin: Little Bay)	PH_02
				23/01/10	Ground, fork by main road to port	LB_01
		Pyroclastic density current deposits (modern)	Trants (Eddie's)	15/01/10	Holding area floor (Tyre tracks)	ED_01
				15/01/10	Finished product: sand, screened (6mm) quarried Nov '09	ED_02
				29/01/10	Sand for block making (origin: Trants)	BF_01
				29/01/10	Rubble/sand from processor floor	BF_02
				23/01/10	Sand shipped out by Eddie's (origin: Trants)	JN_01
			Belham Valley	01/02/10	Crust off processor	BV_01
				01/02/10	Ash coasted sand (stockpile surface)	BV_02
				01/02/10	Non-ash coated sand (deep within stockpile)	BV_03
				?/09/07	Sand from stockpile 2007	BV_04
Greece	Felsic	Pumice (friable, air fall)	LAVA	05/07/10	Fine dust from road near processing area	LA_01
				05/07/10	Raw material from conveyor belt beneath excavated wall	LA_02
				05/07/10	Finished product: screened (0-3 mm) finest grade.	LA_03
				05/07/10	Finished product: screened (0-8 mm)	LA_04
		Perlite (friable, hydrated obsidian)	Aegean	08/07/10	Raw material quarry wall	AP_01
				08/07/10	Finished product: screened (0-1.2 mm)	AP_02
				08/07/10	Finished product: screened (0-3.5 mm)	AP_03
				08/07/10	Finished product: Isoperl Expanded	AP_04
				08/07/10	Finished product: Ergoperl Mix	AP_05
			British Gypsum	Delivered	Raw perlite (Milos, Greece)	BGRP[§]
				29/01/11	Expanded Perlite (expanded in the UK)	BGEP[§]

4.3.2 Sample Selection of <1mm 'bulk' fraction

Bulk compositions of two to five samples of unprocessed material from each quarry were analysed by XRF to determine magma type (processed material may have been winnowed, thereby potentially altering its bulk composition); this ensured that a wide range of magmatic compositions and associated potential hazards (iron-bearing minerals, crystalline silica) were considered for this study.

All samples were analysed for grain size in order to determine which samples contained the highest proportions of respirable material, in order that inferences about potential hazard can be made between different sample types.

Samples from intermediate and felsic quarries – as determined by the XRF analyses – may contain crystalline silica and were analysed by XRD to semi-quantitatively determine the quantity of quartz, cristobalite and tridymite. As Flat Top quarry lies in the Tagihua Ophiolite Complex it was also analysed as tholeiitic basalt may contain some crystalline silica in the groundmass due to silica oversaturation.

Morphology was investigated for samples with the highest quantity of respirable material.

4.3.3 Separation of PM10 and Sample Selection

Eleven samples of the sieved <1mm bulk fraction were selected to have their PM10 (particulate with less than 10µm aerodynamic diameter) component separated for further analyses. Whilst utilising the <1mm fraction for the analytical techniques undertaken in this study allows for comparison with previously published data it is important that certain health-critical parameters are also assessed on a more lung-pertinent fraction (see Chapter 1). Those samples which were most haemolytic (as described in Chapter 5) were selected for size separation, along with some less reactive samples from similar magma types for comparison, to determine whether elevated haemolysis was replicated in the respirable fraction.

These samples were separated at Cardiff University in a 'tumbler' designed by Tim Jones. A sample was placed into an enclosed rotating drum with a unidirectional airflow

pumped via a CAPEX L2C Charles Austen pump at a rate of 10 l/min. As the drum rotates the sample is re-suspended due to disturbance from ridges on the drum's surface. The finer fraction is sufficiently buoyant that the air current draws it into a smaller chamber where the larger particles fall out. The fraction of the sample that is small and low density enough to continue in the airflow enters a Negretti elutriation filter which is designed to allow material <PM10 to pass through, for particulate of an 'average' density (Moreno *et al.*, 2005), which is finally deposited on a Millipore Isopore Membrane filter of 0.6 µm porosity. Samples were run for approximately 24 hours, with the entire apparatus cleaned and dried between sample runs. The separated <10 µm fraction was analysed for grain size, to confirm that a lung-pertinent fraction had successfully been separated from the <1 mm bulk sample; these results showed that all samples had >80 cu. vol% of the ≤10µm fraction and 100 cu. vol. % in the ≤15µm fraction (see graph in Appendix II).

These samples were analysed by XRD to assess their crystalline silica content, as previous studies on volcanic ash from dome collapse material have found crystalline silica enrichment in the finer fraction (Horwell *et al.*, 2003b) probably due to size and density fractionation during dome rock fragmentation within PDCs (Horwell *et al.*, 2001). They were also analysed by SEM to determine their morphology including their aspect ratio which helps to determine the presence of elongate particles, such as fibres, which are potentially more hazardous than other morphologies (Chapter 2, Section 2.6.2). Finally, haemolysis (see Chapter 5) was also conducted on these PM10 samples .

An overview of which analyses were conducted on each sample, both <1mm and ≤10µm, is presented in Tables 4.4 and 4.5 overleaf.

OVERLEAF: Table 4.4 Overview of volcanic quarry samples analysed: X-Si = crystalline silica quantification, ≤10µm = separation, [§]analysed by Jonathan Close except for ≤10µm separation, *obtained from collection of Claire Horwell.

Type	Quarry Sample	Grain Size	Surface Area	Morphology	Composition	X-Si	≤10µm
Mafic	BY_01	√	√	√	√	√	√
	BY_02	√		√	√	√	
	BY_03	√					
	BY_04	√					
	FT_01	√	√	√	√	√	√
	FT_02	√				√	√
	FT_03	√	√	√	√		
	P2_01	√	√	√	√	√	
	P2_02	√	√	√			
	P2_03	√			√		
	P2_04	√					
	P2_05	√				√	
Inter-mediate	PH_01	√	√	√	√	√	√
	PH_02	√	√	√	√	√	√
	LB_01	√					
	ED_01	√		√	√	√	
	ED_02	√	√		√	√	
	BF_01	√				√	
	BF_02	√					
	JN_01	√	√	√			
	BV_01	√	√		√	√	
	BV_02	√		√	√	√	
	BV_03	√	√			√	
	BV_04	√				√	
Felsic	LA_01	√		√	√		
	LA_02	√	√		√	√	
	LA_03	√			√		
	LA_04	√			√	√	
	AP_01	√			√	√	
	AP_02	√	√		√	√	
	AP_03	√					
	AP_04	√					
	AP_05	√			√		
	BGRP[§]	√	√		√		
	BGEP[§]	√	√	√	√		
	AT_01	√					
	AT_02	√					
	AT_03	√			√		
	AT_04	√	√	√	√	√	
	AT_05	√					
	OBS_01[§]	√		√			
	OBS_02[§]	√					
	OBS_03[§]	√		√			√
	OBS_04[§]	√		√	√		
	OBS_05[§]	√		√	√		
	TP_01	√					
	TP_02	√					
	TP_03	√					
	TP_04	√	√	√	√	√	√
	TP_05	√	√	√	√	√	√
	TP_06	√					
	TP_07	√					
	TP_08	√					

Table 4.5 Overview of non-volcanic quarry and volcanic ash samples analysed: X-Si = crystalline silica quantification, PM10 = separation, [§]analysed by Jonathan Close except for PM10 separation, *obtained from collection of Claire Horwell.

Type	Quarry Sample	Grain Size	Surface Area	Morphology	Composition	X-Si	PM10
Greywacke	HU_01	√	√				
	HU_02	√			√		
	HU_03	√	√		√	√	√
	HU_04	√				√	
Sandstone	MSRaw	√	√		√	√	√
	MSCrist	√	√		√	√	√
Type	**Ash Sample**	**Grain Size**	**Surface Area**	**Morphology**	**Composition**	**X-Si**	**PM10**
Mafic	CerNeg*	√	√		√		
	Etna*	√	√		√		
	V1872*	√	√		√	√	
	V1906*	√	√		√	√	
	Fuego*	√	√		√	√	
	Eyja_13*	√			√		
Inter-mediate	SHV_23	√	√	√	√		
	SHV_28	√	√	√	√		
	SHV_99*	√	√		√		
	SHV_03*	√	√		√		
	Pina*	√			√		
Felsic	Chai_02*	√	√	√	√	√	
	Chai_05*	√		√	√	√	

4.3.4 Major Element Composition

The major element oxide compositions of quarry dust and volcanic ash samples were determined by X-ray fluorescence. A representative sub-sample of ~4g was obtained for analysis (as described previously). This sub-sample was powdered in an agate pestle and mortar and dried overnight at 105^{o}C, to remove adsorbed volatiles. Samples were ignited at 950^{o}C for 1.5 hours in a muffle furnace and cooled in a dessicator. They were weighed before and after ignition and cooling, to determine loss on ignition (LOI):

$$LOI = 100 * (W2 - W3)/(W2 - W1) \quad \textbf{Equation 4.1}$$

Where *W1* is the weight of the crucible, *W2* the weight of the crucible with the sample before ignition and *W3* is the weight of the crucible with the sample after ignition. A tetraborate flux (80% Li metaborate; 20% Li tetraborate) was added to the ignited samples at a ratio of 1:5 sample to flux. Weight loss from the flux (in the form of water)

was measured to ensure accuracy of the ratio mixed, by weighing the flux prior to, and after, heating (on a Spartan gas burner) and cooling. Next, 3g of flux (plus any adjustment to account for water loss) was mixed with 0.6g of ignited sample in a crucible. The mixture was heated on a Spartan gas burner to melt and fuse it; the mixture was agitated during this process to ensure that bubbles were removed and all particles were incorporated. The mixture was homogenised by swirling over a Meker gas burner, then reheated on a fusion burner and poured into a heated casting dish. The disc of liquid was then cooled under a forced air cooling system until the disc parted from the casting dish and the fused bead was then allowed to cool to room temperature. Crucibles and casting dishes were made of Pt/Au and handled with titanium-tipped tongs.

Major element analysis was performed on fused beads to eliminate mineralogical effects (e.g. preferential orientation, sample homogeneity) and reduce the inter-element effects. Analyses were conducted using the default PANalytical SuperQ conditions on the PANalytical Axios Advanced X-Ray Fluoresence (XRF) spectrometer (4Kw rhodium anode end window super sharp ceramic technology X-Ray tube) in the Geology Department at the University of Leicester. Instrumental conditions were chosen to avoid any significant line overlaps within the usual compositional range of most geological materials. Stability of the current generation X-Ray Spectrometry systems is determined by running selected suitable drift monitoring samples at the start of each analytical run and calibrations are made by analysing 70-75 international reference materials under the same conditions and regressing the measured count ratios against the recommended concentrations (GeoREM reference site with Philips-based fundamental parameters correction technique). Two to four samples from each quarry were analysed to ensure the results accounted for natural variation within the deposit.

4.3.5 Grain Size

The grain size distribution (GSD) of the dust samples sieved to <1 mm was determined by laser diffraction granulometry (also known as Low Angle Laser Light Scattering (LALLS)) using a Malvern Mastersizer 2000 with Hydro MU and ultrasonic attachment. The dust particles diffract light at an angle that is inversely proportional to their size, and the angles of diffraction detected are used in conjunction with Mie theory to determine

particle size distribution (details of the process are presented in Appendix II). The measurement requires four assumptions to be made regarding the material analysed (Mishchenko & Travis, 2008):

i) That all particles are spherical.

ii) That all particles have a homogeneous and equivalent density.

iii) That the optical properties of the particles are known, i.e. the real & imaginary components of the refractive index (RI).

iv) That there is no error in the intensity distribution.

The first two assumptions are unlikely to exactly reflect the quarry dust studied which potentially introduces small errors into the measurements obtained; however, whilst the particles were not spherical they were morphologically similar (as observed by SEM) which negates the need for specialist instrumentation (Eshel *et al.*, 2004). For the third assumption, the optical properties were determined on the basis of their magma type (as determined by elemental composition) following the method for volcanic ash as described by Horwell (2007). For the real part of the refractive index, 1.55 was selected for the mafic samples (up to 55 wt. % SiO_2) and 1.63 for the intermediate and felsic samples (above 55 wt. % SiO_2). This is in keeping with a study by Horwell (2007) which found that the RI for basaltic ash with an SiO_2 content of ~ 55 wt. % can be expected to fall in the range of 1.54–1.56 and for andesitic ash, RIs of 1.56 and 1.63 were both found to give similar GSDs (therefore both are close to the optimal RI) (Horwell, 2007). As an RI of 1.63 has been used previously for the Soufrière Hills ash and other andesitic and dacitic samples (Horwell, 2007), it was also selected for the intermediate and felsic samples in this study. During the calculations using the Malvern Instruments software, it is possible to vary RI so different RIs were tested here (results in Appendix II) but the optimal RIs were in agreement with Horwell (2007). For the imaginary part of the refractive index (absorption coefficient, AC) a value of 0.1 was used, which is the same as used by Horwell (2007) for volcanic ash. Horwell tested different ACs ranging from 0 to 1 and found that the GSDs for ash did not vary for AC = 0.1-1 but significantly underestimated the respirable fraction for AC = 0.

The 1-2 mm size fraction range was re-incorporated into the grain size distribution using the mass of the sieved fraction following the methods of Horwell (2007), as the definition of ash includes all particles <2mm but only the <1mm fraction can be analysed

by laser diffraction due to instrument limitations (Horwell, 2007) which also addresses potential errors introduced by sieving. The data were then converted to cumulative % and interpolated to give health-pertinent cut-offs (Chapter 2, Figure 2.4) as the Mastersizer's automated binning does not give these exact bins.

A representative sub-sample from the <1mm sieved fraction of each sample was taken by gently inverting the sample container (to counteract size segregation due to settling) and then cone-and-quartering the whole sample to obtain a representative ~5g. The sample was dispersed in water (sample added in small increments until the appropriate obscuration was achieved) and grain size distributions (GSD) measured with the following standard operating procedure: measurement time: 10s; average of: 3 cycles; snaps: 10,000; obscuration range: 5-20%; pump speed: 2500; ultrasonic displacement: 10. These are the same parameters which are routinely used to determine the GSD of volcanic ash (Horwell, 2007) and therefore aids in keeping the results comparable (as described in aim 4, Chapter 1). Each sample was run three times and results averaged. After each run, results were compared and, where the curves (from the distribution graphs) did not overlie each other, a new sample was run and the average taken from six measurements. Nine samples were selected at random, representing each magma type, along with a non-volcanic comparison and re-run to assess data reproducibility; very little difference between the sets of runs was observed (the maximum was 3.4 cu.vol.% at 10 μm). These data are presented in Appendix II. For particles with an aerodynamic diameter of <0.02μm the reporting accuracy of the Malvern Mastersizer is less than for particles of a larger size (i.e. not as good as the 1% accuracy and variation in reporting for >0.02μm); however, no particles of this small size formed part of the sample here.

Samples of the separated PM10 fraction and the obsidian samples were analysed using a Beckman-Coulter LS230 Laser Diffraction Particle Size Analyzer with PIDS (Polarization Intensity Differential Scattering) which works using Fraunhofer light theory instead of Mie theory and, therefore, does not require RI data. Samples were run with the following parameters: 10-12 % obscuration; 30s of sonication and a 90s run time. Samples were suspended in glycerol rather than water following investigations by J. Close into differences in results between the two instruments which were carried out on three samples (Close, 2012). It was found that the Coulter LS consistently reported a higher wt.

% of each fraction in all samples and that this difference was minimised by suspending samples in glycerol. The grain size distributions reported by the Coulter LS can be better calibrated to those of the Mastersizer using the equation:

$$y = 0.7766x - 0.8078 \qquad \textbf{Equation 4.2}$$

This equation was developed by Close from these comparisons (with an R^2 value of 0.9903), where x is the wt. % for each fraction reported by the Coulter LS and y is the approximate wt. % of the same fraction as the Mastersizer would have reported it. The Mastersizer-calibrated results are presented in this chapter for the <1mm and both sets of results (Coulter and Mastersizer) for the PM10 fraction.

4.3.6 Specific Surface Area

The surface area of the quarry samples was determined by using the Brunauer Emmett Teller (BET) method of gas adsorption (Brunauer *et al.*, 1938). Representative sub-samples were obtained by cone and quartering, until a sample of ~5g remained. This sub-sample was weighed and placed into a glass tube with a bulb of 0.5 inches in diameter at the base, and placed into a Micromeretics FlowPrep instrument for heating at 150^{o}C with nitrogen gas blowing over the sample for a minimum period of 2 hours. The heat ensured any adsorbed moisture or other volatile contaminants were removed from the particles and the gas flow removed them from the tube itself. The samples were then re-weighed to account for any volatile loss. The sample tubes were placed into an isothermal jacket (to prevent gradients of temperature during analysis) and a glass filler rod was placed inside them. The tubes were loaded into ports on a Micromeretics TriStar 3000 (which takes three tubes simultaneously) and their respective weights entered into the software. The samples are placed under vacuum into liquid nitrogen with the sample reaching the same temperature as the nitrogen gas, so that nitrogen adsorption could take place. The nitrogen gas was administered and the accumulated gas quantity and gas pressure data measured and collected providing an adsorption isotherm.

For this analysis, data for the first part of the isotherm were collected along 10 points of relative pressure (ranging from 0.05-0.30 p/p^{o}) to increase accuracy (Sing, 1982). All results with a minimum correlation co-efficient of 0.999 and a margin of error of

<0.05m^2/g were accepted and no negative c-values (negative intercepts) were observed. Each sample was analysed three times to account for sample heterogeneity, with a new sub-sample analysed each time. Calibration was run using the reference standards: silica-alumina, carbon black and kaolinite of known surface area, all of which yielded results well within the instrument's detection limit.

4.3.7 Particle Morphology and Semi-Quantitative Elemental Composition

Scanning electron microscopy (SEM) was used to observe the morphology of particles and to semi-quantitatively assess particle elemental composition for unusual or fibre-like particles. Samples were analysed in a Hitachi SU-70 FEG SEM equipped with Oxford Instruments INCA analysis system (EDS) at the GJ Russell Microscopy Facility, Department of Physics, Durham University, with an accelerated voltage of 12 kV. Samples of dust from the <1mm fraction were sprinkled on to carbon sticky pads using a spatula. The carbon pads were adhered to 12 mm diameter aluminium stubs and the stubs were coated to a thickness of ~25 nm using carbon for elemental analysis and a platinum-gold alloy for morphological analyses. Calibration was run prior to each session of EDS using cobalt for the beam current (as it is the most stable element) which gives 10k cps accuracy and repeatability, and a detection limit of 0.2 wt%.

All samples which had appreciable concentrations of respirable material (see results section 4.4.3) were imaged and analysed. Material on the stubs was observed using a raster pattern across the area of the stub (on the order of 80-100 particles or aggregates per observation) of which 15-25 representative particles were imaged in SE mode, as well as any potentially morphologically-significant, fibre-like ones, or any which were particularly small; these were also subject to elemental analysis EDS. The isolated PM10 fraction of samples separated by tumbling were studied in greater detail, with aspect ratio measured for ~1000 particles per sample in order to quantify morphologies. ImageJ software was used to calculate the long axis and orthogonal short axis of each particle in order to determine the aspect ratio shape factor which was calculated by dividing the short axis by the long axis. An average for each sample was obtained where elongate morphologies gave results near-zero and equiaxed morphologies near-unity.

In order to determine whether crystalline silica particles were un-occluded at their surfaces and free to react with the lung, or whether the surfaces were coated in any adhering minerals, as observed by Horwell et al. (2012) at the Soufrière Hills volcano, dust samples collected at the Montserrat quarries were mounted in resin, polished and observed in cross-section by SEM and analysed with EDS. Only Montserrat samples were chosen as none of the other quarries investigated had deposits containing substantial amounts of crystalline silica. Resin blocks were made by combining a liquid epoxy resin (5:1 ratio of resin to epoxy hardener) with around 2g of a representative sub-sample of dust. Once the resin had hardened (overnight) the blocks were ground on silicon-carbide grit paper, rinsed in acetone and then polished with a finer grit paper (6 μm, then a 1 μm slurry finish). Finally the surface was carbon coated (~25 nm), and silver dag was applied from the edge of the coating to the block holder to earth the sample and prevent charging.

4.3.8 Crystalline Silica Quantification

The presence of crystalline silica polymorphs was determined semi-quantitatively by X-ray Diffraction (XRD) using the Internal Attenuation Standard (IAS) method (Le Blond *et al.*, 2009). The wavelength of the X-rays is similar to the distance between atoms in crystals (i.e. bond length) and as minerals are defined by their structure and composition, no two minerals will have identical powder diffraction patterns; therefore, identification of minerals based on their diffraction peak positions (indexing) can be made using an index of pure powder patterns (details of the XRD process are given in Appendix II). In the IAS method, the addition of a known quantity of standard into the sample (as a pseudo-binary mix) allows for semi-quantification of the mineral phases present in weight per cent, without first determining the mineralogy of the sample. The known quantity of IAS added is then compared to the quantity detected by XRD in the pseudo-binary mix through pattern fitting and mass attenuation coefficient is calculated. This coefficient is a measure of how intensely a mineral either absorbs or scatters light at a specific wavelength per unit of mass, and is obtained from equation 4.3.

In the IAS method, a bulk attenuation coefficient is determined for the multi-phase natural sample:

$$W_{IAS} = [X_{IAS}\ (\mu/\rho)']/[(\mu/\rho)_{IAS}] \qquad \textbf{Equation 4.3}$$

where W_{IAS} is the weight of the internal attenuation standard added to the sample (where 1- W_{IAS} is the weight of the sample) and $(\mu/\rho)_{IAS}$ is its known mass attenuation coefficient. X_{IAS} is the pattern fit value determined by comparing the pure IAS pattern with the pattern from the pseudo-binary mix. The mass attenuation coefficient of the pseudo-binary phase $(\mu/\rho)'$ can be determined thus:

$$(\mu/\rho)_{sample} = [(\mu/\rho)_{IAS}\ W_{IAS}\ (1/\ X_{IAS}\ -1)]/[1-\ X_{IAS}] \qquad \textbf{Equation 4.4}$$

where W_{IAS} is the weight fraction of the IAS in the pseudo-binary mix and $1\text{-}X_{IAS}$ is the weight fraction of the sample. X_{IAS} is the phase pattern fit for the IAS estimated with a pattern-fitting analysis programme (e.g. LINKFIT). Following this, the weight percent of any single phase of interest is obtained:

$$W_i = [X_i\ (\mu/\rho)_{sample}]/[(\mu/\rho)_i] \qquad \textbf{Equation 4.5}$$

where $_i$ denotes the phase of interest, hence W_i is the weight % of the phase of interest and X_i is the pattern intensity of the phase of interest within the sample mix. $(\mu/\rho)_{sample}$ is the mass attenuation coefficient of the sample (without the added IAS). Le Blond et al. (2009).

A representative sub-sample was obtained as described previously and powdered in an agate pestle and mortar to homogenise the sample grain size. The powdered sample was loaded into an Al circular 'deep well' mount (volume 180 mm^3) and packed with the knife side of a spatula to create a flat but roughened surface thereby reducing potential for preferential orientation on the sample surface (Batchelder & Cressey, 1998).

Phases of interest which were run alongside the dust samples include: quartz, cristobalite and tridymite as well as labradorite an intermediary (50-70% An) mineral in the plagioclase series. Labradorite was run because the XRD pattern has peak overlap with cristobalite near 21° 2θ and it is often the dominant mineral in magma of intermediate to felsic composition; therefore, its signal needed to be removed prior to analysis of cristobalite and tridymite for accurate quantification. ZnO was used as an internal attenuation standard (IAS) because it is not naturally present in volcanic samples

(hence there is little peak overlap in the XRD patterns) and has a similar attenuation coefficient to the samples under investigation. Analyses were run on a static position sensitive detection (XRD-sPSD) using an Enraf-Nonius PSD 120 2θ Diffractometer with Inel detector and a Genex high-power source; $Cu_{K\alpha 1}$ radiation was selected with a germanium (III) monochromator and the tube operating conditions were set at 45 kV and 45 mA. The horizontal and vertical slits were adjusted to 0.24 by 5.0 mm, respectively, and the beam reflection onto the sample was kept at 12^{o} to the horizontal. NBS silicon powder and silver behenate were used as external 2θ calibration standards. 2θ linearization was carried out using a cubic spline function with Enraf-Gufi software and calibration performed daily. The data collection time for each pattern acquisition was 10 minutes during which samples were constantly rotated on the horizontal plane.

The IAS method is semi-quantitative and reports an error of -/+ 3 wt.% (Le Blond et al. 2009) based on the cumulative effects of both instrument error and user error (i.e., those associated with sample preparation and interpretation of diffraction patterns). This margin of error is carried over from the predecessor peak-stripping technique (Batchelder and Cressey 1998), and was further corroborated for the IAS method with a trial of ten synthetic mixtures with known quantities of each mineral phase (Le Blond *et al.*, 2009). Inherent instrument error is constrained as far as possible by adhering to the settings and calibrations detailed above; however, the cumulative error associated with the user and their samples can be introduced over several steps. These factors are described in Table 4.6.

As peak stripping can be a subjective process, several individuals from the research group analysed data from the same XRD runs and compared results, in order to confirm the margin of error associated with the technique. These results varied amongst users, displaying consistency in either over- or under- estimating phases of interest from similar sample types (e.g. volcanic ash from a single source); but, were found to be within the -/+ 3 wt.% margin of error associated with the technique itself, although larger errors were associated with quantifying greater amounts of a phase of interest.

Table 4.6 Factors which may contribute to cumulative user error for the semi-quantitative IAS method of crystalline silica quantification.

Factor	How it may contribute to cumulative user error
Sample heterogeneity	Complex multi-phase samples may have more complicated diffraction patterns in comparison to more homogenous samples.
Sample homogenisation	Samples are ground prior to analysis in order to homogenise their grain size. A lack of complete homogenisation may lead to slight differences in the diffraction angle (for example, by introducing preferred orientation).
Sample packing	Ground samples should be packed into an Al circular mount, with the knife edge of a spatula to give flat but slightly roughened surface. The density of sample packing can alter the extent to which the X-ray beam can penetrate into the sample. This is corrected for by the phase attenuation coefficient, but relies on the volume of the packing to be constant. A roughened surface discourages preferred orientation on the surface as a random orientation of crystals is required in the deep well.
Poor mixing with IAS	Samples must be thoroughly mixed with a measured quantity of the ZnO (IAS) which requires care as mixed natural dusts exhibit a different density to the ZnO. Poor mixing may result in differences between the amount of ZnO detected, compared to the known amount added.
Peak integration	This is a subjective process which differs amongst individual users and may lead to bias in the form of over- or under- estimation of phases.

Currently, work is continuing to reduce this error further by using more accurate standards, i.e. phases of interest separated directly from a sample of the heterogeneous natural dust being analysed; and increasing both peak overlap and peak definition, which would allow for more accurate quantification of phases of interest in a heterogeneous sample (Damby, 2013). Further steps to reduce the margin of error might include grinding

the sample to a particular sieve mesh size to ensure that a consistent grain size is achieved.

Determining absolute figures for instrument error and detection limits for this technique is challenging, with the age of the X-ray tube and any fluctuations in gas flow potentially contributing to drift in instrument readings over time. To account for this, the instrument was calibrated daily prior to use, by running a NBS silicon and a silver behenate standard of known chemical composition which together cover the full range of $^{o}2\theta$ and allow for any adjustments in shift to be accounted for.

Around half of the analyses here were repeated on new sub-samples (i.e. run in duplicate) and several different samples from each quarry location were selected to ensure that natural variation was accounted for and a representative quantification obtained (as shown in Table 4.5).

4.4 Results <1mm Fraction

4.4.1 Major Element Composition

The results of the XRF analyses are presented in Figure 4.2 in the total alkali vs. silica classification scheme of Le Maitre (1989). Figure 4.3 classifies basaltic rocks by potassium content, which is relevant here because tholeiitic basalts can contain small amounts of quartz (Le Maitre, 1989). It can be seen that the sites chosen successfully cover much of the spectrum of major magma compositions and certainly represent different SiO_2 concentrations. The XRF data for the comparative ash samples were obtained from published work; samples included Vesuvius, Etna (Horwell *et al.*, 2010b), Soufrière Hills, Cerro Negro, Fuego, Pinatubo (Horwell *et al.*, 2007) and Eyjafjallajökull (Horwell *et al.*, 2013a) (see Table 4.4 for sample information).

The samples from Flat Top quarry (FT_01 and FT_03) are close to the calc-alkaine and tholeiitic boundary. This is in keeping with the results of other studies which have found that the lavas of the Tangihua Ophiolite Complex are relatively homogeneous, primarily comprised of tholeiitic basalts with minor calc-alkaline and alkaline affinities (Nicholson *et al.*, 2000).

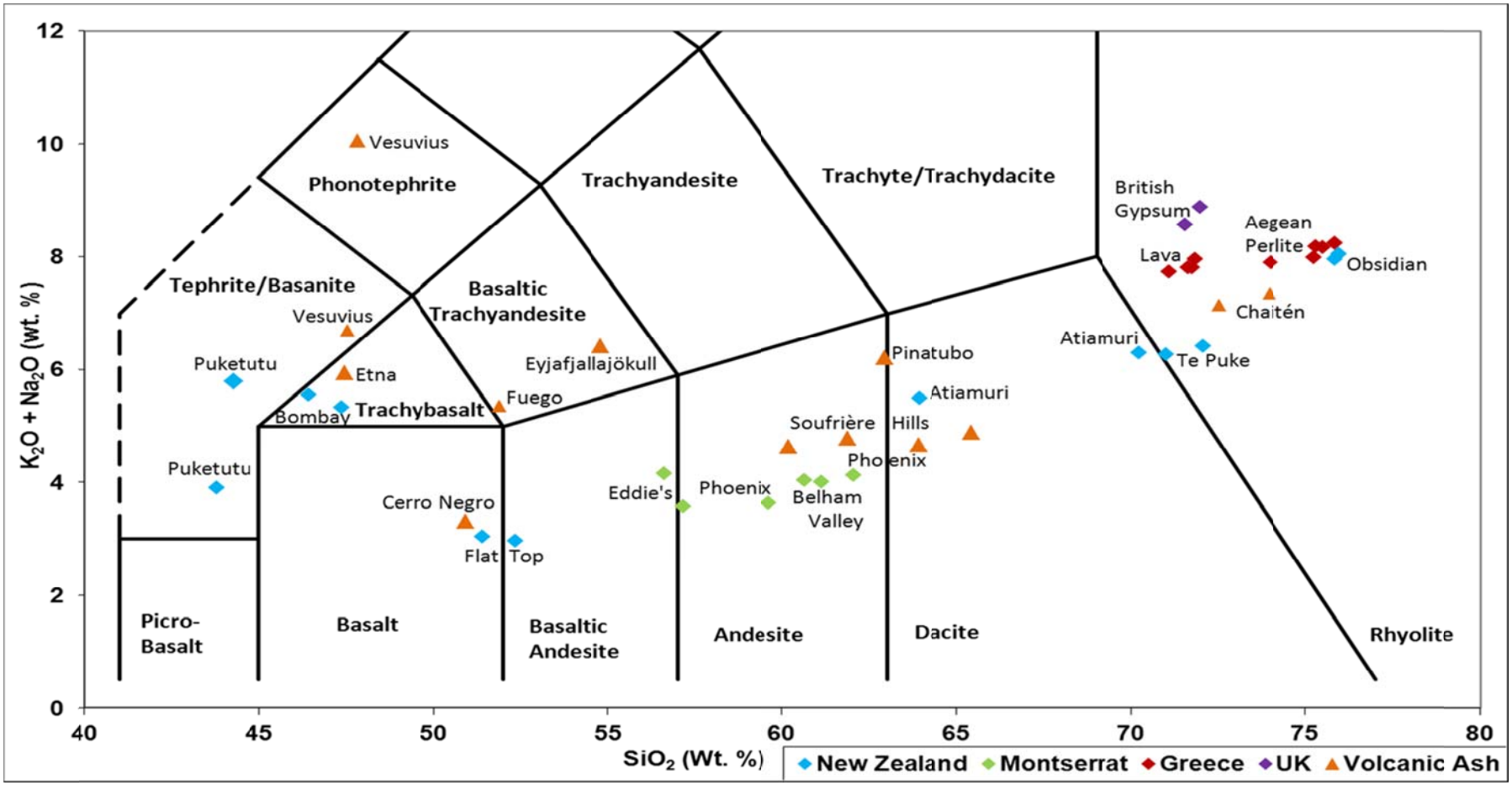


Figure 4.2 Total Alkali versus Silica (TAS) plot to show magma types of volcanic quarry dust and ash samples. Separated into three broad categories: mafic, intermediate and felsic, denoted in grey.

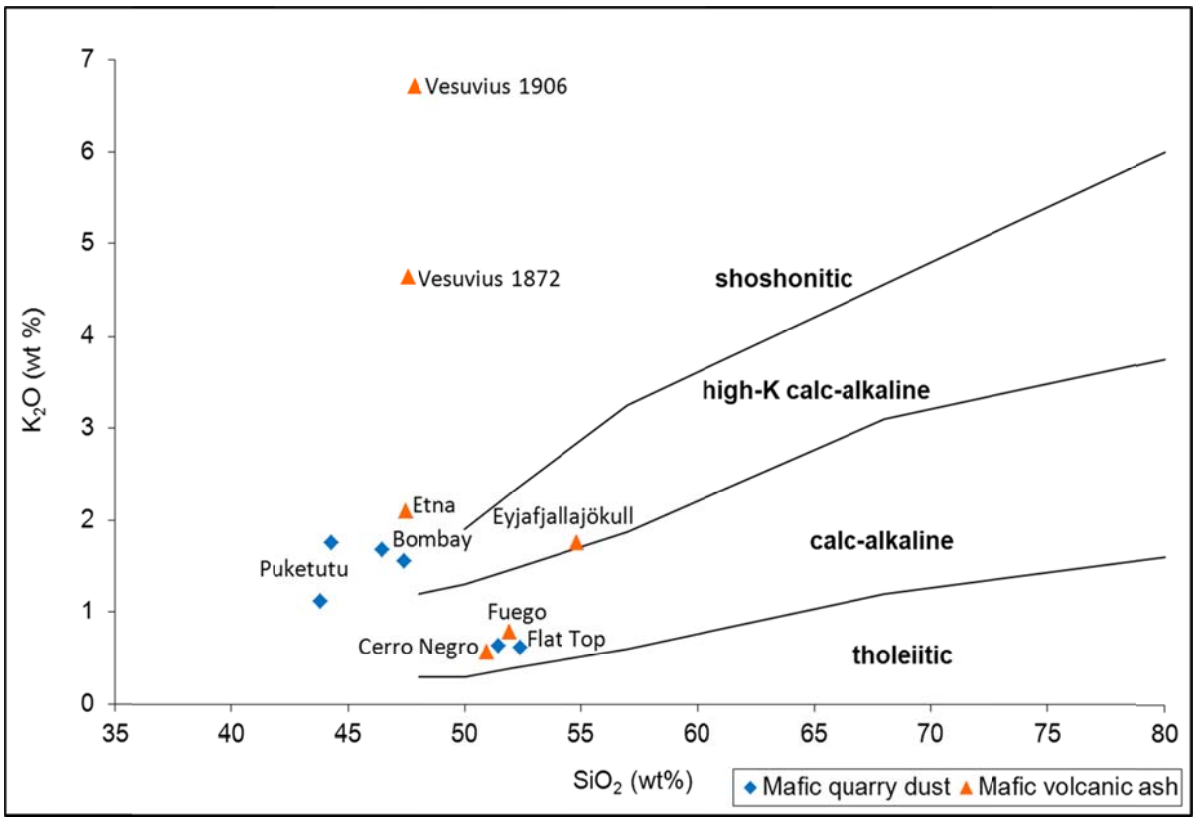


Figure 4.3 The classification of mafic magmas of Le Maitre (1989).

The elemental composition of each of the samples is shown in Table 4.7 for volcanic quarried material and Table 4.8 for the non-volcanic quarried material and the volcanic ash samples. The Puketutu samples contain comparatively high levels of both MgO and CaO, with the MgO being characteristic of the primitive lava of the Auckland Volcanic Field, whilst the CaO may be due to the presence of augite (which is abundant in the groundmass) (McGee Lucy, 2012). The current Soufrière Hills eruption has shown consistent variation in bulk chemistry since the beginning of the eruption (Murphy *et al.*, 2000). However, from these XRF data there is little elemental difference between material quarried from the Silver Hills ancient complex (PH_01 and PH_02), Trants (ED_01 and ED_02) and the Belham Valley (BV_01 and BV_02).

Loss on ignition (LOI) is controlled by a sample's mineralogy, with higher LOI exhibited by samples possessing a higher volatile content; fresh quartz, olivine, pyroxene and feldspars have virtually no volatiles whereas micas and sheet silicates often carry 2-3 wt.% volatile components and amphiboles, chlorites and clays can carry up to 4-5 wt.% (Marsh, 2013). This mineralogy-volatile association can be seen in the basaltic samples from Bombay (prefixed "BY") and Puketutu ("P2"), which are low in

volatiles and LOI (typically comprised of olivine, pyroxene and feldspar); whilst the ancient samples from Flat Top ("FT") have over 4 wt.% LOI and are likely to contain clays which have weathered from feldspars (confirmed by XRD in Chapter 5). Similarly, the freshest (most recently erupted) intermediate samples from Monserrat come from the Belham Valley (BV) which have very low LOI compared to many of the older, more weathered samples from Trants (ED) or Little Bay (PH) which contain up to 2.4 wt.%.

Table 4.7 XRF data in oxide weight % for volcanic quarry samples. BDL = below detection limit.

Magma Type	Sample	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	SO_3	LOI	Total
Mafic	**BY_01**	47.38	2.36	14.09	13.87	0.21	8.24	7.61	3.78	1.55	0.73	BDL	0.6	100.41
	BY_02	46.46	2.50	13.68	14.34	0.21	8.19	7.95	3.87	1.68	0.72	BDL	0.4	100.01
	FT_01	52.38	1.43	14.41	12.50	0.20	4.13	7.53	2.36	0.61	0.12	BDL	4.5	100.15
	FT_03	51.44	1.40	14.68	12.78	0.21	4.37	7.73	2.40	0.63	0.11	0.10	4.14	99.97
	P2_01	43.81	2.85	12.29	14.05	0.18	13.10	10.04	2.78	1.12	0.43	BDL	0.14	100.79
	P2_03	44.28	3.30	14.09	13.35	0.18	8.68	9.62	4.04	1.75	0.59	BDL	0.21	99.65
Intermediate	**PH_01**	59.66	0.47	18.60	5.88	0.22	1.50	6.83	3.11	0.53	0.12	BDL	2.44	99.35
	PH_02	62.07	0.53	17.86	6.95	0.23	1.53	5.90	3.47	0.65	0.16	0.10	1.19	100.63
	BV_01	60.68	0.86	16.86	7.96	0.17	2.63	6.78	3.21	0.83	0.12	BDL	0.32	100.42
	BV_02	61.17	0.64	16.68	7.81	0.20	3.05	6.68	3.18	0.82	0.12	BDL	0.32	100.67
	ED_01	57.18	0.85	17.69	8.82	0.22	3.04	7.06	3.01	0.57	0.12	BDL	2.18	100.73
	ED_02	56.63	0.68	19.34	8.16	0.19	2.58	8.19	3.46	0.69	0.12	0.01	0.20	100.24
Felsic	**LA_01**	71.87	0.12	12.04	1.23	0.04	0.33	1.40	3.67	4.28	0.01	0.00	5.60	100.61
	LA_02	71.65	0.13	12.06	1.19	0.04	0.37	1.90	3.58	4.22	0.01	<0.002	5.76	100.91
	LA_03	71.13	0.13	11.90	1.19	0.04	0.44	2.20	3.58	4.15	0.01	<0.002	5.66	100.43
	LA_04	71.79	0.13	12.03	1.20	0.04	0.35	1.85	3.57	4.24	0.01	<0.002	5.33	100.54
	AP_01	74.03	0.13	12.11	1.13	0.04	0.14	0.81	3.67	4.22	0.01	<0.002	3.84	100.14
	AP_02	75.32	0.12	12.25	1.09	0.04	0.12	0.70	3.77	4.40	0.01	<0.002	2.54	100.36
	AP_05	75.53	0.12	12.24	1.07	0.04	0.14	0.70	3.73	4.43	0.01	<0.002	2.47	100.46
	AP_07	75.87	0.13	12.29	1.05	0.04	0.06	0.67	3.72	4.51	0.01	<0.002	2.08	100.43
	AP_08	75.26	0.13	12.40	1.12	0.04	0.11	0.76	3.65	4.33	0.01	0.02	2.71	100.53
	BGRP	71.57	0.19	13.57	1.61	0.05	0.22	0.68	3.12	5.44	0.05	<0.002	3.39	99.91
	BGEP	72.00	0.20	13.97	1.65	0.07	0.43	0.64	3.24	5.64	0.06	<0.002	1.72	99.61
	AT_03	63.95	0.73	15.16	6.28	0.16	1.87	3.96	4.05	1.44	0.07	0.02	1.02	98.71
	AT_04	70.27	0.46	14.02	4.02	0.13	0.95	2.38	3.99	2.31	0.07	BDL	2.33	100.94
	TP_04	71.05	0.37	14.58	2.74	0.08	0.53	2.21	3.77	2.50	0.03	BDL	2.73	100.60
	TP_05	72.09	0.23	12.59	1.69	0.07	0.39	1.27	3.13	3.29	0.01	BDL	4.10	98.86
	Obs_05	75.88	0.19	13.02	1.72	0.062	0.16	1.07	4.71	3.247	0.021	<0.002	0.38	100.45

Table 4.8 XRF data (oxide weight %) for non-volcanic quarried samples and volcanic ash samples. Data obtained from published sources: [*] (Horwell *et al.*, 2007) , [+] (Horwell *et al.*, 2010b), [#] (Horwell *et al.*, In press) [§] (Horwell *et al.*, 2008) all run on same instrument.

Type	Sample	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	SO_3	LOI	Total
Greywacke	HU090302	62.33	0.92	15.80	6.52	0.11	2.52	3.70	4.25	2.38	0.17	BDL	1.86	100.55
	HU090303	58.63	0.75	17.44	6.43	0.10	3.06	4.27	2.27	2.28	0.20	BDL	4.82	100.26
Sandstone	MSRAWE	90.51	0.20	4.10	1.57	0.09	0.08	0.00	0.08	1.22	0.02	<0.002	1.02	98.88
	CRISTOB	98.41	0.06	0.60	0.03	0.01	0.03	0.00	0.24	0.35	0.00	<0.002	0.19	99.90
Mafic	Cerro Negro[*]	50.94	0.93	17.22	12.37	0.21	4.92	10.38	2.74	0.57	0.14	BDL	-0.23	100.18
	Etna[*]	47.46	1.73	16.72	11.56	0.17	5.72	10.10	3.84	2.10	0.61	BDL	-0.18	99.84
	Fuego 74[*]	51.90	0.85	19.35	9.37	0.14	3.35	8.77	4.58	0.79	0.19	BDL	0.23	99.51
	Vesuvius 1872[+]	47.57	1.01	12.51	8.30	0.13	8.08	14.49	2.06	4.64	0.80	BDL	0.09	99.67
	Vesuvius 1906[+]	47.86	0.75	16.35	8.00	0.14	4.89	10.05	3.34	6.71	0.71	BDL	0.75	99.57
	Eyjafjallajökull_13[#]	54.81	1.71	13.85	10.28	0.22	2.35	5.25	4.67	1.75	0.40	BDL	3.12	98.43
Intermediate	Pinatubo[*]	62.97	0.45	16.75	4.11	0.10	2.54	5.66	4.91	1.30	0.21	BDL	0.79	99.78
	Montserrat 99[*]	63.92	0.52	15.60	6.18	0.15	2.34	5.85	3.78	0.87	0.15	BDL	0.42	99.79
	Montserrat 03[*]	61.91	0.56	16.37	6.57	0.15	2.34	6.33	3.86	0.92	0.15	BDL	0.46	99.63
	MA_23	65.47	0.54	15.60	5.73	0.14	2.32	5.66	3.68	1.20	0.12	<0.002	0.09	100.55
	MA_28	60.23	0.60	17.99	6.63	0.15	2.47	7.28	3.67	0.96	0.12	<0.002	0.19	100.29
Felsic	Chai_02[§]	72.55	0.18	13.79	1.88	0.066	0.45	1.76	4.19	2.958	0.068	0.12	1.07	99.08
	Chai_05[§]	73.98	0.15	13.79	1.53	0.055	0.22	1.50	4.31	3.048	0.060	0.00	0.67	99.31

4.4.2 Grain Size Analysis

The samples were analysed for their grain size distribution and here the cumulative volume per cent of the health-pertinent fractions are presented. Cumulative volume per cent (cu. vol. %) allows for the total amount of particulate to be observed at any of the health-relevant cut-offs. Although the sub-100 µm fraction is deemed as inhalable, the data here are presented to 15 µm because it allows for a clearer display of the finer fraction which is of greater relevance for chronic health (coarser particles are also likely to be cleared from the lungs much more rapidly).

As outlined in section 4.1, the main aims are to explore the variation in grain sizes both within and amongst different quarries and processes, and to explore whether analogies can be drawn between volcanic ash and volcanic quarry dust. The first sets of graphs (Figures 4.5-4.7) show the variations in grain size distributions in cu.vol.% with each figure depicting a different magmatic composition (mafic, intermediate and felsic); the dust sample types (raw, drilled, quarry floor etc.) are shown for each quarry.

Figure 4.5 shows the grain size distribution at three mafic quarries (A-C) and a greywacke quarry (D) in New Zealand. The latter is included because the method of extraction and processing is the same as in the mafic quarries (extraction from solid rock). The samples are a mixture of drilled fines (resulting from the drilling of holes for blasting), blasted fines (collected following the blast and comprised of a mixture of drilled fines and new fragments created by the blast) and finished product (which has been crushed and screened). In all of the quarries it can be observed that drilled fines contain the greatest amount of respirable material (<4µm), typically 4-8 cu.vol.%, followed by blasted fines or the finished product which contained 2–6 cu.vol.% sub-4 µm material. Overall, dust from all quarries contains <8 cu.vol.% sub-4 µm material, with the exception of one sample from Bombay quarry (Figure 4.6 A), namely BY_01, which contains 12 cu.vol.%.

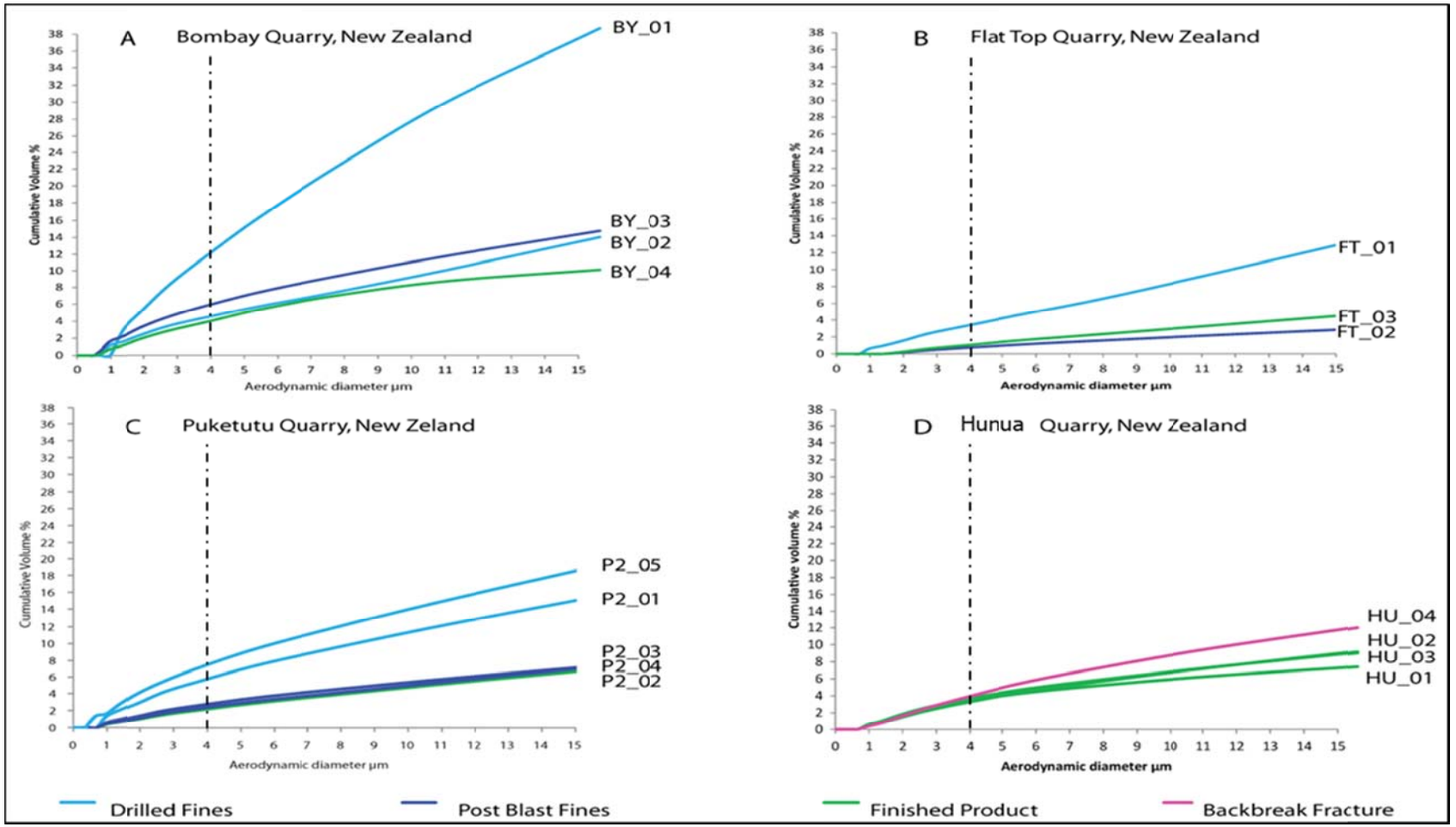


Figure 4.5 Grain size distributions of dust to 15 µm from three mafic quarries (A-C) and one greywacke quarry (D). The greywacke data include a sample of dust from the backbreak fracture (HU_04; a layer of volcanic ash in the deposit exposed during the blast).

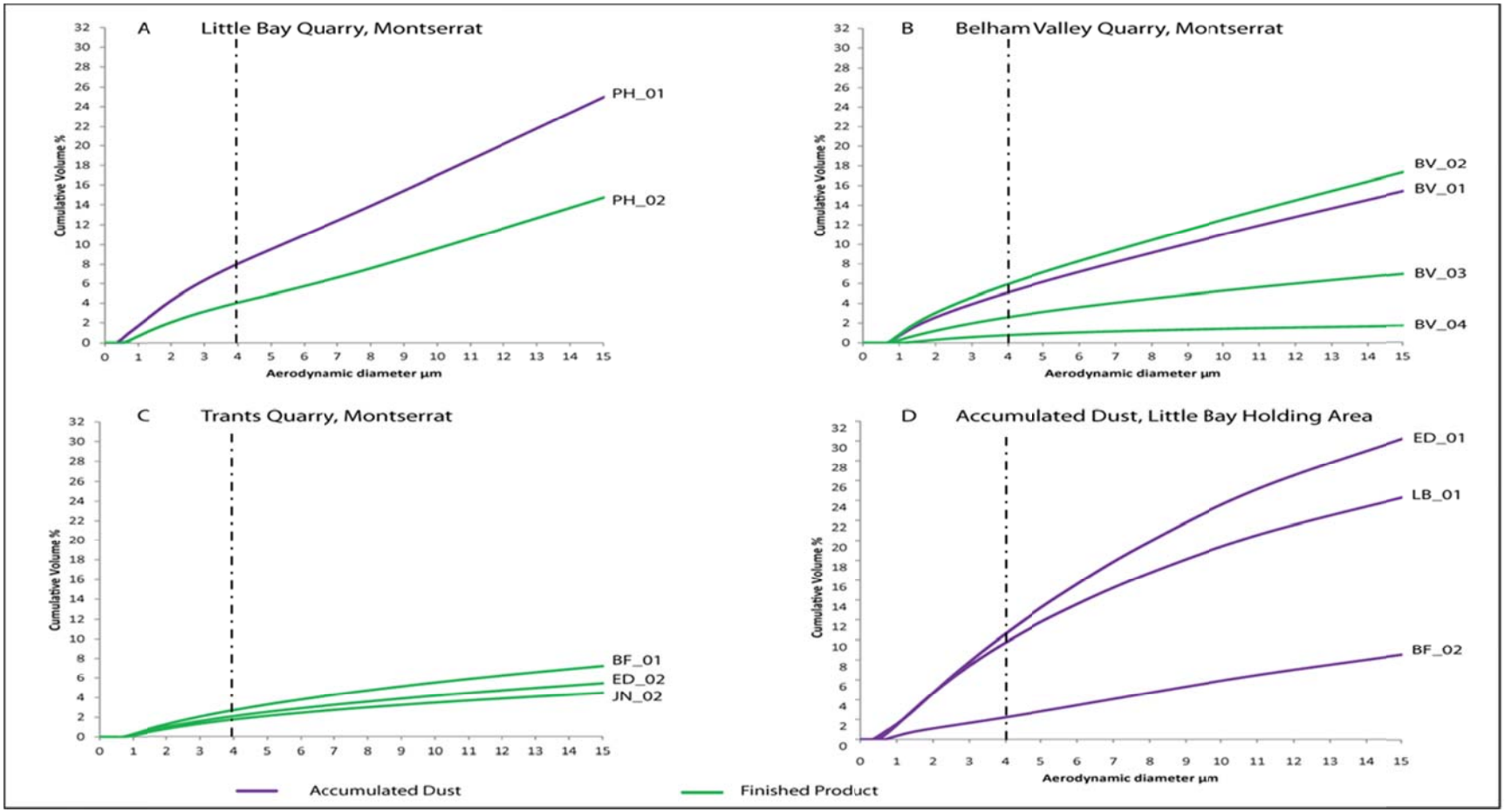


Figure 4.6 Grain size distributions to 15 µm of accumulated dust (purple) and finished product (green) in three intermediate quarries on Montserrat (A-C) and accumulated dust in the Little Bay holding area (D).

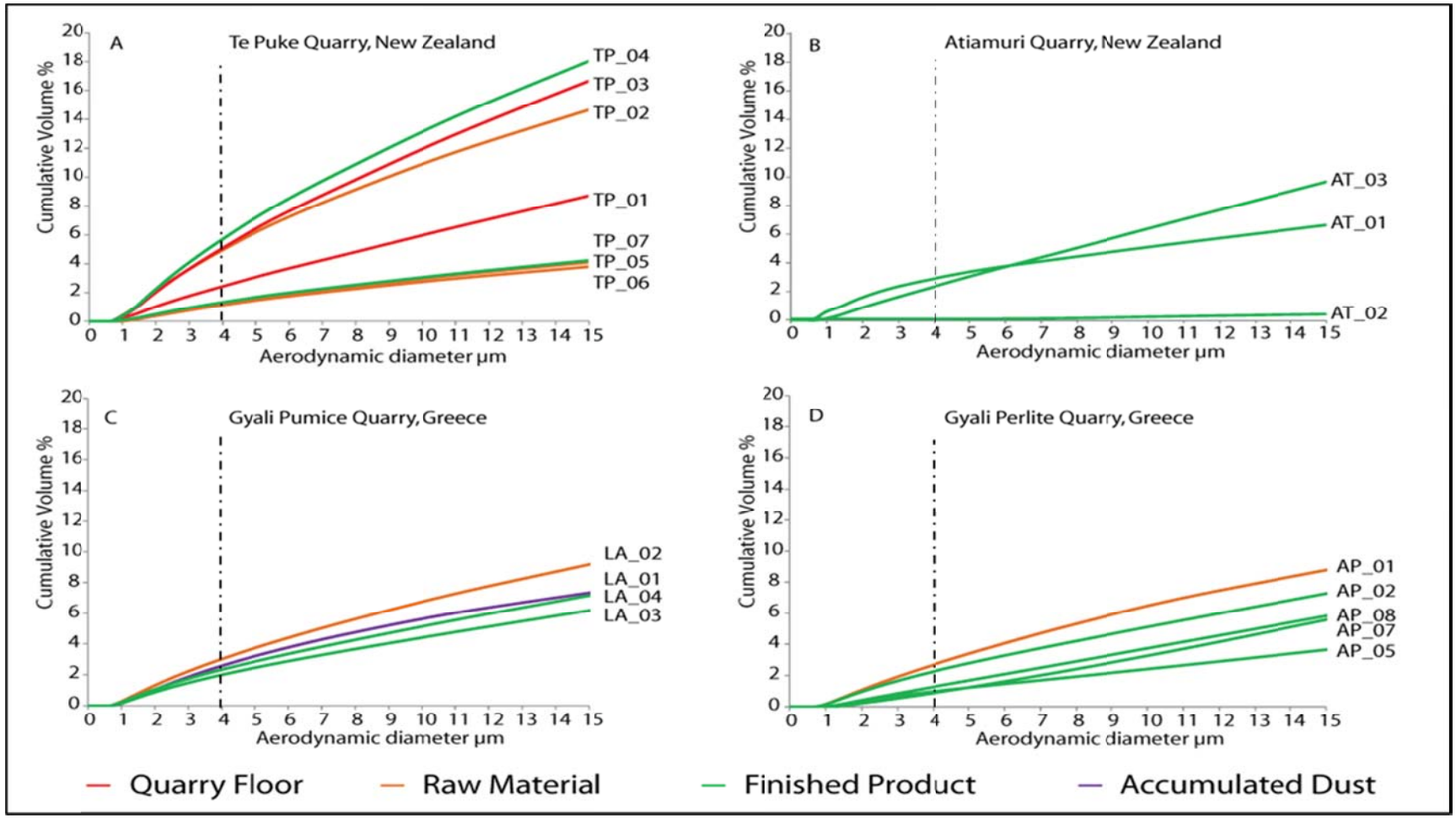


Figure 4.7 Grain size distributions of dust to 15 µm from two felsic quarries in New Zealand (A-B) and two felsic quarries in Greece (C-D).

Figure 4.6 shows the grain size distribution from three quarries (A-C) which mined andesitic material on Montserrat and a graph of accumulated dust from the Little Bay holding area (D) where finished product is stored in stockpiles prior to being shipped overseas. The results showed variation in respirable material both among samples within the same quarry and among different quarries. Overall, the accumulated dust (on the processor) was finer than that contained in the finished product, with all samples of finished product containing <4 cu.vol.% sub-4 µm material with the exception of sample BV02 (figure 4.6 B) which was taken from the top of the stockpile and may be contaminated by ashfall. The finest samples of accumulated dust were in the Little Bay holding area (ED01 and LB01, figure 4.6 D) and both contained ~10 cu.vol.% sub-4 µm material.

Figure 4.7 shows grain size distribution of dust from two felsic quarries extracting pumice in New Zealand (A-B) and two felsic quarries in Greece extracting pumice (C) and perlite (D). There was considerable variation in the quantities of respirable dust from samples of raw material, from the quarry floor, in the finished product and in accumulated dust, with no systematic pattern amongst quarries. Three of the samples from Te Puke quarry in New Zealand contain more fine particles (in cu.vol.%) than all other felsic samples from the Greek quarries and the Atiamuri quarry in New Zealand. These samples (TP_02, TP_03 and TP_04), which were from raw material, quarry floor and finished product respectively, have ~6 cu.vol.% sub-4 µm material in comparison to <3 cu.vol.% for the other samples including similarly sourced samples from the same quarry.

Figure 4.8 presents the same data as in Figures 4.5-4.7 but is displayed by processing method rather than by magma type. Re-displaying the results in this way illustrates clearly that the unprocessed (raw, friable felsic) samples are coarser than drilled and blasted, mafic samples. It is also clear that finished product can span almost the entire range of distributions (0.1–6.2 cu.vol.% sub-4 µm). Accumulated dust can vary greatly even within the same magmatic type (0.2–11.3 cu.vol.% sub-4 µm), but it is worth noting that mafic processors had little accumulated dust due to the washing procedure and so samples could only be collected from felsic and intermediate processors.

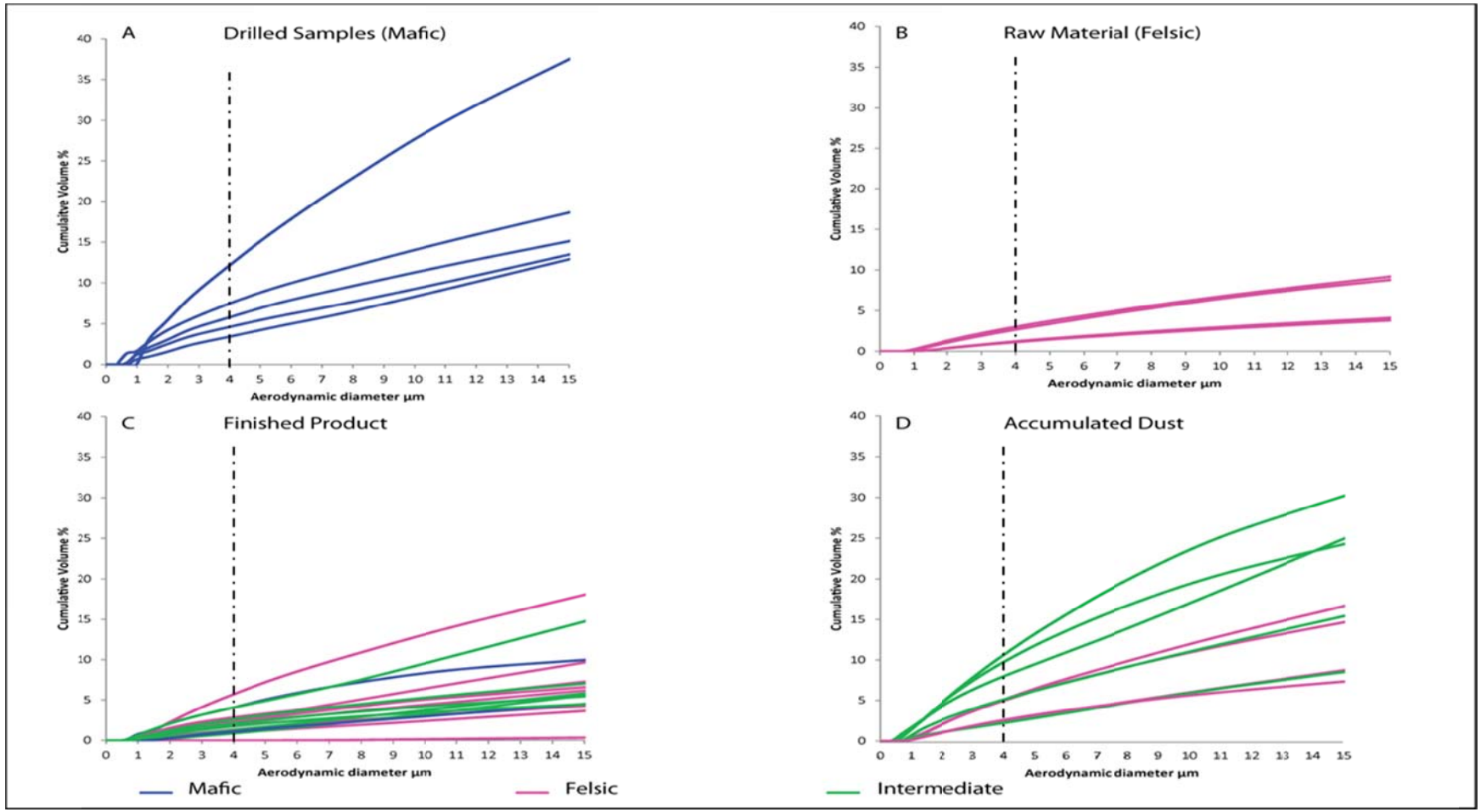


Figure 4.8 Grain size distributions of dust samples to 15 µm displayed by sample type: A Raw (Drilled and blasted) Mafic; B Raw (including quarry floor) Felsic; C finished, processed product; D Accumulated dust (i.e. on processor). The magma type is indicated by colour.

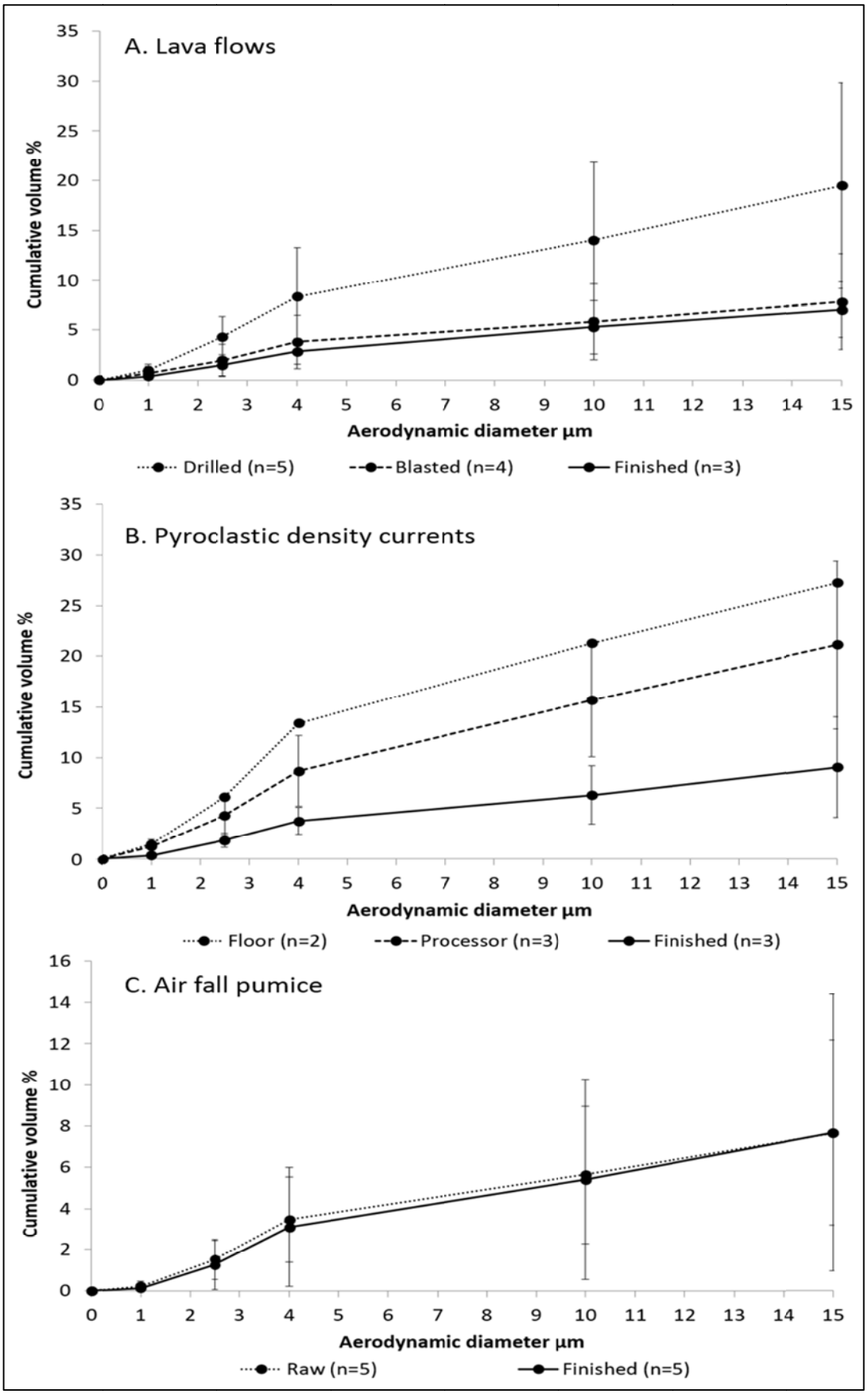


Figure 4.9 The average ≤15 µm of different sample types at quarries extracting: a) lava flows (Bombay, Flat Top and Puketutu); b) pyroclastic density currents (Eddie's, Phoenix and Belham Valley); and c) air fall pumice (Lava, Te Puke and Atiamuri). Error shown is 1σ.

Figure 4.9 compares selected different sample types of quarry dust grouped according to their mode of emplacement; a) lava flows, b) pyroclastic density currents and c) air fall pumice by average grain size distribution to ≤15 μm. There is very little difference between these sample types, however, given the extent of the error (1 standard deviation), which highlights the range of variability both within and between quarries, even for the same sample type.

Figure 4.10 compares the quarry dust samples with volcanic ash of the same magmatic groupings: mafic, intermediate and felsic. For each graph, the volcanic ash data are displayed as an envelope which encompasses the range of published data available for that style of eruption (Damby *et al.*, 2013, Hillman *et al.*, 2012, Horwell, 2007, Horwell *et al.*, 2013a, Horwell *et al.*, 2010a, Horwell *et al.*, 2010b, Le Blond *et al.*, 2010) (see Appendix II for all ash samples within the range). Overall, for the mafic samples, the quarried samples fell within the range expected for volcanic ash; however, one sample of drilled fines was substantially finer than the ash samples. The intermediate quarried samples had a similar distribution to volcanic ash: the finest quarry dusts were accumulated dusts (purple lines) and were comparable to the finest ash (from dome collapse events). The dust in the intermediate quarried finished product was generally coarser than volcanic ash, with some samples being coarser overall than the coarsest ash types. The felsic quarried dusts, which include the samples of obsidian analysed by J. Close, were much coarser than volcanic ash of comparable magmatic origin, with few samples of accumulated dust bearing comparison to the coarsest examples of ash.

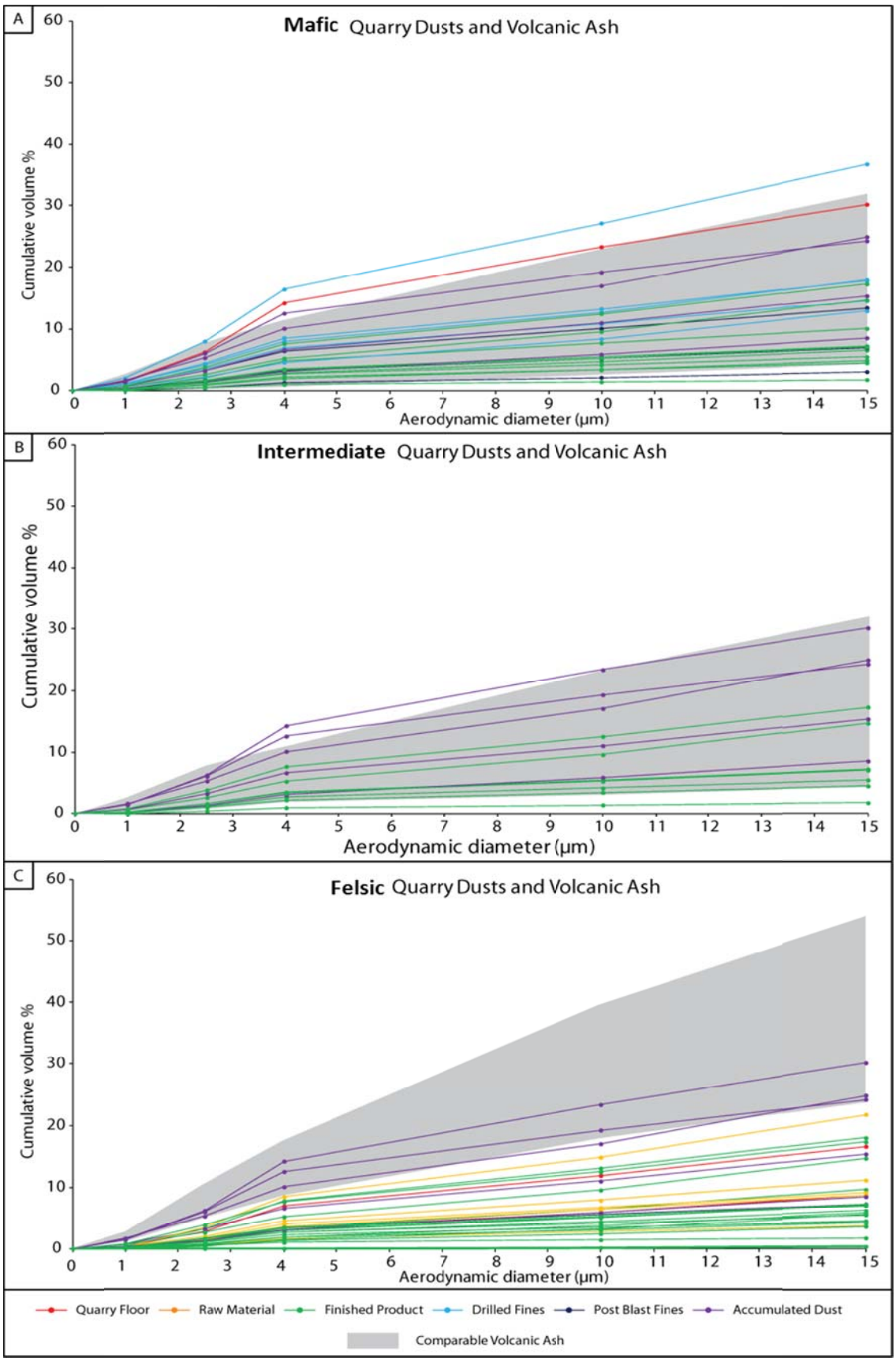


Figure 4.10 Grain size distribution of quarry dusts (colour coded by sample type) and volcanic ash (grey envelope (Damby *et al.*, 2012, Hillman *et al.*, 2012, Horwell, 2007, Horwell *et al.*, In press, Horwell *et al.*, 2010a, Horwell *et al.*, 2010b, Le Blond *et al.*, 2010)) of the same magmatic composition.

Finally, the grain size distributions are presented in tabular form for ease of comparison of the respirable content for different samples, in Tables 4.9 and 4.10. Additional samples of volcanic ash of specific interest to this study (i.e. selected for comparative analysis of crystalline silica content) are also presented in this table. The tables indicate that the ultra-fine fraction (that is, <1µm) of the quarry dust varies amongst samples, with felsic samples having almost no material in the fraction (a maximum of 0.4 cu.vol.% from three Te Puke samples) whilst most mafic and intermediate samples) contain slightly greater amounts (up to 1.7 cu.vol%). The ultra-fine fraction within the volcanic ash samples exhibited the broadest variation, range 0.0-2.7 cu.vol.%, indicating that some samples contain an appreciable quantity of ultra-fines. Aside from one sample of ash from Vesuvius (violent strombolian eruption of 1906, with 2.7 cu.vol.% of <1µm material) the finest ash samples are from Montserrat (also up to 2.7 cu.vol.%). In summation, for volcanic ash, intermediate samples overall contain the most respirable material, whereas, both mafic and intermediate quarry dust samples contain ultra-fine material.

Table 4.9 Origin and quantity of <15µm cu.vol. % for quarry dust samples. All samples analysed by author except those indicated [+] which were analysed by Chris Rolfe (Malvern Mastersizer, Cambridge University) and [§] which were analysed by J. Close (Coulter LS, Durham University, calibrated to the Malvern Mastersizer size fractions).

Magmatic grouping	Quarry	Sample Number	Sample Type	<1 µm	<2.5 µm	<4 µm	<10 µm	<15 µm
Mafic	Bombay	BY_01	Drilled (exhaust)	0.2	7.4	12.2	27.5	37.5
		BY_02	Drilled	1.2	3.2	4.6	9.3	13.5
		BY_03	Post-blast	1.7	4.2	6.0	11.0	14.3
		BY_04	Finished (7 mm)	0.8	2.6	4.1	8.2	10.0
	Flat Top	FT_01	Drilled	0.6	2.1	3.4	8.3	12.9
		FT_02	Post-blast	0.0	0.3	0.8	2.0	2.9
		FT_03	Finished (25 mm)	0.0	0.5	1.1	3.0	4.5
	Puketutu	P2_01	Drilled	1.3	3.9	5.8	11.3	15.1
		P2_02	Finished (20 mm)	0.4	1.4	2.3	4.8	6.7
		P2_03	Post-blast	0.5	1.6	2.5	5.0	7.0
		P2_04	Post-blast	0.6	1.9	2.8	5.4	7.1
		P2_05	Drilled	1.7	5.1	7.5	14.0	18.6
Intermediate	Trants	ED_01	Quarry Floor	1.5	6.3	10.6	23.3	30.2
		ED_02	Finished	0.2	1.3	2.1	4.1	5.4
		BF_01	Finished	0.3	1.6	2.7	5.5	7.2
		BF_02	Quarry Floor	0.3	1.4	2.2	5.9	8.5
		JN_01	Finished	0.1	1.1	1.7	3.4	4.5
	Little Bay	PH_01	Accumulated	1.7	5.3	8.0	17.0	24.9
		PH_02	Finished	0.6	2.6	4.1	9.6	14.7
		LB_01	Quarry Floor	1.4	6.1	9.7	19.2	24.3
	Belham Valley	BV_01	Accumulated	0.7	3.3	5.1	11.0	15.4
		BV_02	Finished (surface)	0.8	3.8	5.9	12.5	17.4
		BV_03	Finished (deep)	0.3	1.6	2.6	5.3	7.0
		BV2007	Finished	0.0	0.4	0.8	1.4	1.7

Magmatic grouping	Quarry	Sample Number	Sample Type	<1 µm	<2.5 µm	<4 µm	<10 µm	<15 µm
Felsic	Te Puke	TP_01	Quarry Floor	0.2	1.4	2.4	6.0	8.7
		TP_02	Raw Material	0.4	2.9	5.0	10.9	14.7
		TP_03	Quarry Floor	0.4	2.9	5.1	11.9	16.7
		TP_04	Finished (4 mm)	0.4	3.2	5.7	13.1	18
		TP_05	Raw material (ash)	0.0	0.6	1.2	3.0	4.1
		TP_06	Raw material (pumice)	0.0	0.6	1.1	2.7	3.8
		TP_07	Finished (2 mm)	0.1	0.7	1.3	3.1	4.2
	Atiamuri	AT_01	Finished (perlite)	0.5	1.9	2.8	5.0	6.6
		AT_02	Finished (4 mm)	0.0	0.0	0.0	0.1	0.3
		AT_03	Finished (1.9 mm)	0.1	1.3	2.4	6.4	9.7
	LAVA[+]	LA_01	Accumulated	0.1	1.5	2.6	5.6	7.3
		LA_02	Raw	0.3	1.8	3.0	6.7	9.2
		LA_03	Finished (3 mm)	0.1	1.2	2.0	4.4	6.2
		LA_04	Finished (8 mm)	0.2	1.4	2.3	5.1	7.1
	Aegean Perlite[+]	AP_01	Raw	0.2	1.5	2.7	6.4	8.8
		AP_02	Finished (1.2 mm)	0.1	1.3	2.2	5.1	7.3
		AP_05	Finished 3.5 mm)	0.0	0.5	1.0	2.4	3.6
		AP_07	Finished (expanded)	0.0	0.4	0.9	3.3	5.6
		AP_08	Finished (expanded)	0.0	0.6	1.3	3.7	5.8
	Henderson[§]	OBS_01	Raw material	0.0	0.6	1.1	2.9	4.0
		OBS_02	Accumulated	0.0	1.5	2.3	5.1	6.8
		OBS_03	Accumulated	0.3	3.1	4.3	8.7	11.0
		OBS_04	Quarry floor	0.0	1.1	1.6	3.7	5.2
Non-Volcanic: Greywacke	Hanua	HU_01	Finished (5 mm)	0.5	2.2	3.4	5.9	7.3
		HU_02	Post-blast	0.5	2.0	3.3	6.7	9.0
		HU_03	Drilled	0.6	2.4	3.7	6.8	8.9
		HU_04	Post blast (fracture)	0.4	2.3	3.9	8.7	11.7
Non-Volcanic: Sandstone	Moneystone	MS_Raw	Raw material	1.4	19.3	32.2	55.6	67.1
		MS_Crist	Finished product	1.2	4.8	8.4	18.0	22.1

Table 4.10 Details of volcanic ash samples with respect to origin and quantity of <15µm cu.vol. % All analyses conducted by author with the exception of those indicated: [*]Horwell, 2007, [+] Horwell et al, 2010 and [^] Horwell et al, 2012.

Magmatic grouping	Volcano	Eruptive Style	VEI	Grain Size Distribution; Cumulative Volume Per Cent				
				<1 µm	<2.5 µm	<4 µm	<10 µm	<15 µm
Mafic	Fuego, Guatemala 1974[*]	Sub-plinian	4	0.9	2.4	3.7	8.0	12.0
	Cerro Negro, Nicaragua[*]	Strombolian-vulcanian	2	0.0	0.2	0.6	2.6	4.2
	Vesuvius, Italy 1872[+]	Effusive strombolian	3	0.5	1.3	2.2	5.4	7.9
	Vesuvius, Italy 1906[+]	Violent strombolian	4	2.7	7.6	11.2	20.8	27.0
	Etna, Italy[*]	Strombolian	3	0.3	1.1	1.8	4.6	6.8
	Eyjafjallajökull, Iceland 2010[^]	Strombolian	4	0.6	3.3	5.1	13.6	20.0
Intermediate	Soufrière Hills, Montserrat 1999[*]	Dome collapse	3	1.9	6.7	10.7	23.1	31.9
	Soufrière Hills, Montserrat 2003[*]	Dome collapse	3	2.7	7.9	11.5	22.5	30.8
	Soufrière Hills, Montserrat 2010	Ash venting (sample MA23)	3	1.7	4.3	6.1	12.4	17.4
	Soufrière Hills, Montserrat 2010	Ash venting (sample MA28)	3	0.3	1.1	1.6	3.2	4.6
	Pinatubo, Philippines 1991[*]	Sub-plinian	6	1.3	6.2	9.8	18.9	24.3
Felsic	Chaitén, Chile 2008	Explosive, dome collapse	4	1.4	6.6	10.7	21.6	29.0
	Sakurajima, Japan 1471-1476	Plinian (sample Q1)	5	0.7	3.0	5.4	11.4	15.8
	Sakurajima, Japan 1471-1476	Plinian (sample Q2)	5	2.5	9.6	13.6	39.6	59.1
	Sakurajima, Japan 1471-1476	Plinian (sample Q3)	5	2.5	10.8	23.9	46.2	58.6
	Sakurajima, Japan 1471-1476	Plinian (sample Q4)	5	0.3	1.6	3.0	6.5	9.0
	Sakurajima, Japan 1471-1476	Plinian (sample Q5)	5	1.1	3.6	5.5	12.9	19.5
	Sakurajima, Japan 1471-1476	Plinian (sample Q6)	5	2.2	9.1	16.4	39.9	55.5
	Sakurajima, Japan 1471-1476	Plinian (sample Q7)	5	0.1	0.9	1.6	3.9	5.6
	Sakurajima, Japan 1471-1476	Plinian (sample Q8)	5	2.0	6.8	10.5	30.6	48.8
	Sakurajima, Japan 1914	Plinian (sample Q9)	4	0.6	2.4	4.1	9.8	14.4

4.4.3 Specific Surface Area

The specific surface area (Table 4.11) of volcanic quarry dusts varies substantially, ranging from 0.7-10.8 m^2/g. Non-volcanic quarry dusts have a narrower range (1.2-5.6 m^2/g) and volcanic ash also has a small range of 0.3-1.3 m^2/g (although published data range up to ~8 m^2/g (Damby *et al.*, 2012, Horwell *et al.*, 2013a, Le Blond *et al.*, 2010).

Table 4.11 The specific surface area of quarried samples (by magma or rock type). ‡(Horwell *et al.*, 2007). Average of 3 runs, error to 3σ for analyses conducted by author.

Type	Sample	Average specific surface area m^2/g	Standard deviation 3σ
Mafic Quarry Dust	BY_01	3.8	0.1
	FT_01	8.3	3.3
	FT_03	10.8	1.4
	P2_01	1.8	0.5
	P2_05	1.0	0.0
Intermediate Quarry Dust	PH_01	2.3	0.2
	PH_02	4.8	1.4
	BV_01	0.8	0.3
	BV_03	0.7	0.3
	ED_02	0.3	0.3
	JN_01	0.7	0.1
Felsic Quarry Dust	LA_02	0.7	1.4
	AP_02	1.5	0.1
	BGEP	2.0	0.3
	BGRP	1.6	0.1
	AT_04	1.9	0.6
	TP_04	5.1	0.4
	TP_05	3.8	0.0
Sandstone Quarry Dust	MSRaw	1.2	0.2
	MSCrist	2.5	0.8
Greywacke Quarry Dust	HU_01	2.7	0.2
	HU_04	5.6	0.5
Mafic Volcanic Ash	Fuego‡	0.54	-
	Etna‡	0.19	-
	Cerro Negro‡	0.47	-
	V1906‡	1.03	-
	V1872‡	0.19	-
Intermediate Volcanic Ash	MA_23	0.3	0.1
	MA_28	0.1	0.1
	SHV_99	1.28	-
	SHV_03	1.03	-
Felsic Volcanic Ash	Chai_02	1.3	0.2

4.4.4 Particle Morphology and Elemental Composition

The morphology of the <10μm fraction (of the <1mm bulk) of volcanic quarry dusts, non-volcanic quarry dusts and volcanic ash was investigated by SEM. Whole particle morphology was investigated for all sample types, whilst thin-section morphology was investigated for those volcanic quarry dust samples which were found (by XRD) to contain appreciable levels of crystalline silica (>10 wt.%). Quantitative analysis of particle morphology was undertaken for the ≤10 μm fraction of 11 samples which were separated by tumbling.

4.4.4.1 Whole particle morphology

When looking at health-pertinent fractions (<10μm) of mafic, intermediate and felsic quarry dust samples they mostly appear blocky and angular with no distinct crystal forms. Typical morphologies are shown in Figure 4.12 for mafic samples, Figure 4.13 for intermediate and Figure 4.14 for felsic samples.

The morphology of the <10μm fraction of non-volcanic quarry dusts (namely greywacke and sandstone) is shown in Figure 4.15 and is similar to that of the volcanic dusts. Some samples contain material in individual grains but the vast proportion of material is either agglomerates or single larger particles with much smaller particles adhered to them. Several samples of volcanic dust from intermediate and felsic magmas, and greywacke contain sporadic particles of spherical or near-spherical morphology, indicated with red rectangles in Figures 4.13, 4.14 and 4.15. Material from the sandstone quarry (Figure 4.15 B-D) contained platy layered crystals of quartz.

Observations of samples of volcanic ash from volcanoes of similar magmatic composition reveal comparable morphologies, albeit without well-defined crystals (4.16). In general, respirable ash displays a similar angular, blocky morphology, with larger particles hosting aggregates of smaller particles at their surfaces (Damby *et al.*, 2013, Hillman *et al.*, 2012, Horwell *et al.*, 2013a) as shown in Figure 4.22. Occasional chemically-bound aggregates (from transport in the plume) are also observed in volcanic ash (e.g. Figure 3a, (Damby *et al.*, 2012)) which were not observed in the quarry samples.

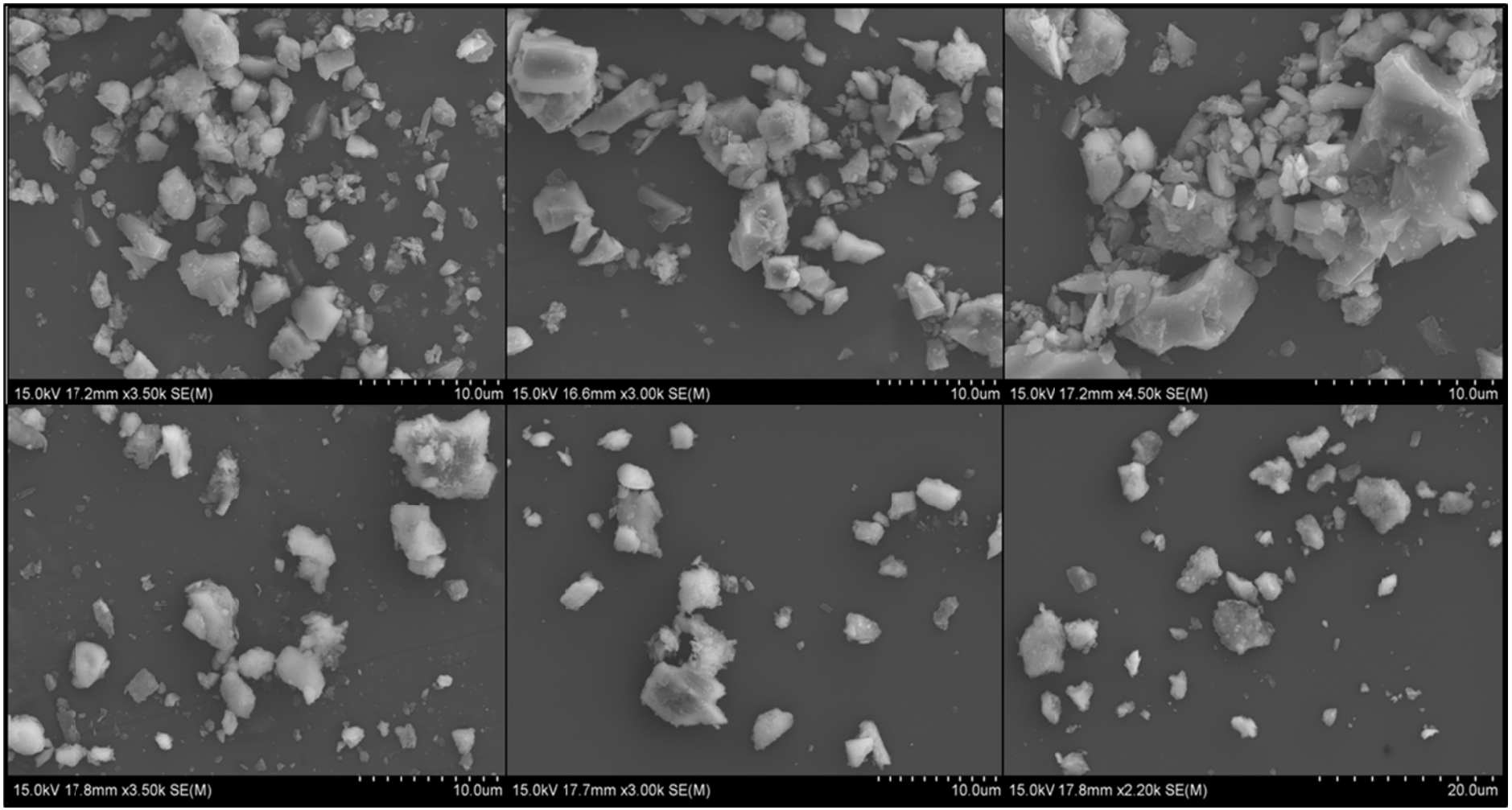


Figure 4.12 Representative SEM images of typically observed morphologies in the respirable fraction of mafic quarry dusts.

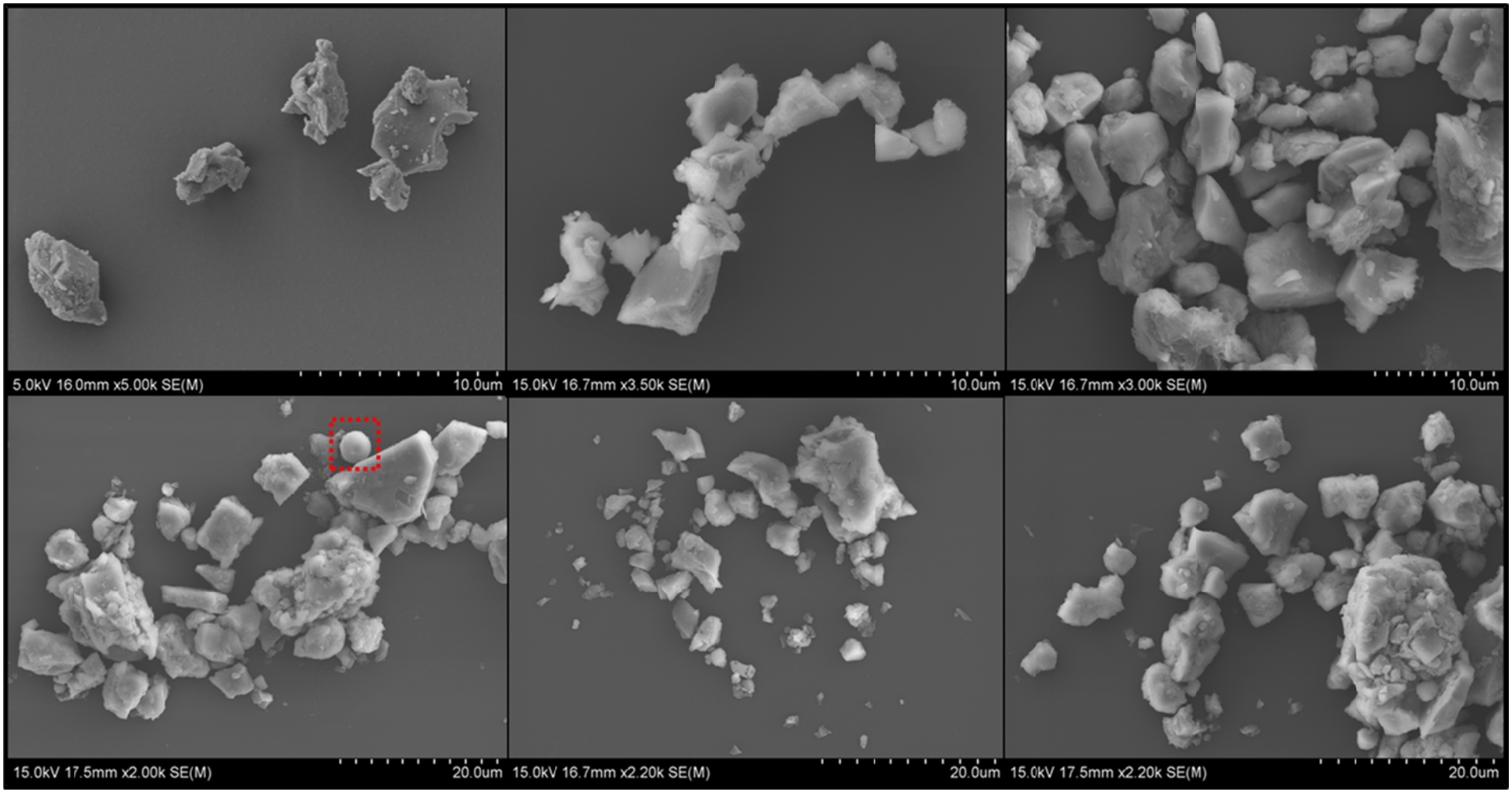


Figure 4.13 Representative SEM images of typically observed morphologies in the respirable fraction of intermediate quarry dusts. Red box shows particle with spherical morphology.

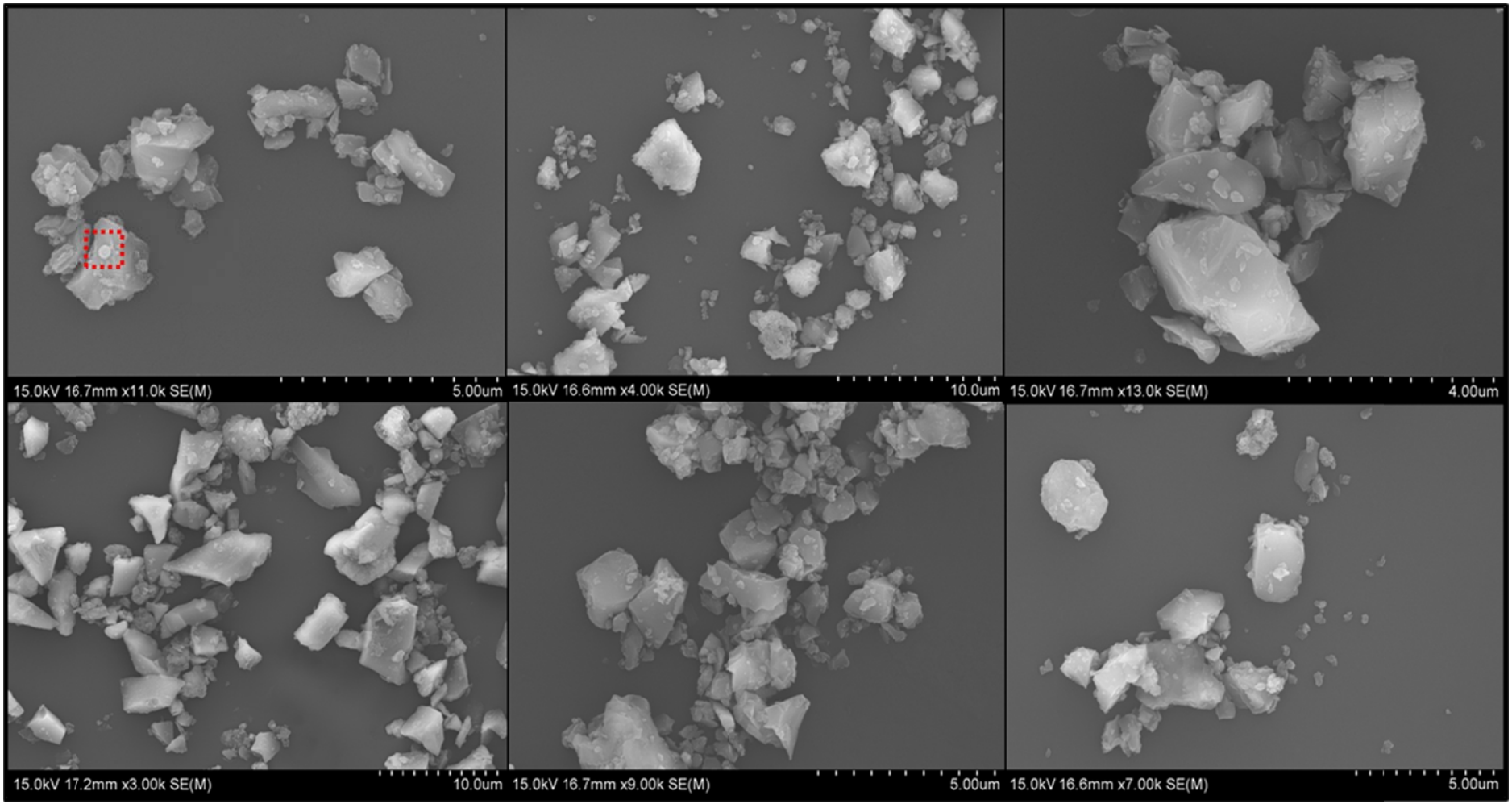


Figure 4.14 Representative SEM images of typically observed morphologies in the respirable fraction of felsic quarry dusts. Red box shows particle with spherical morphology.

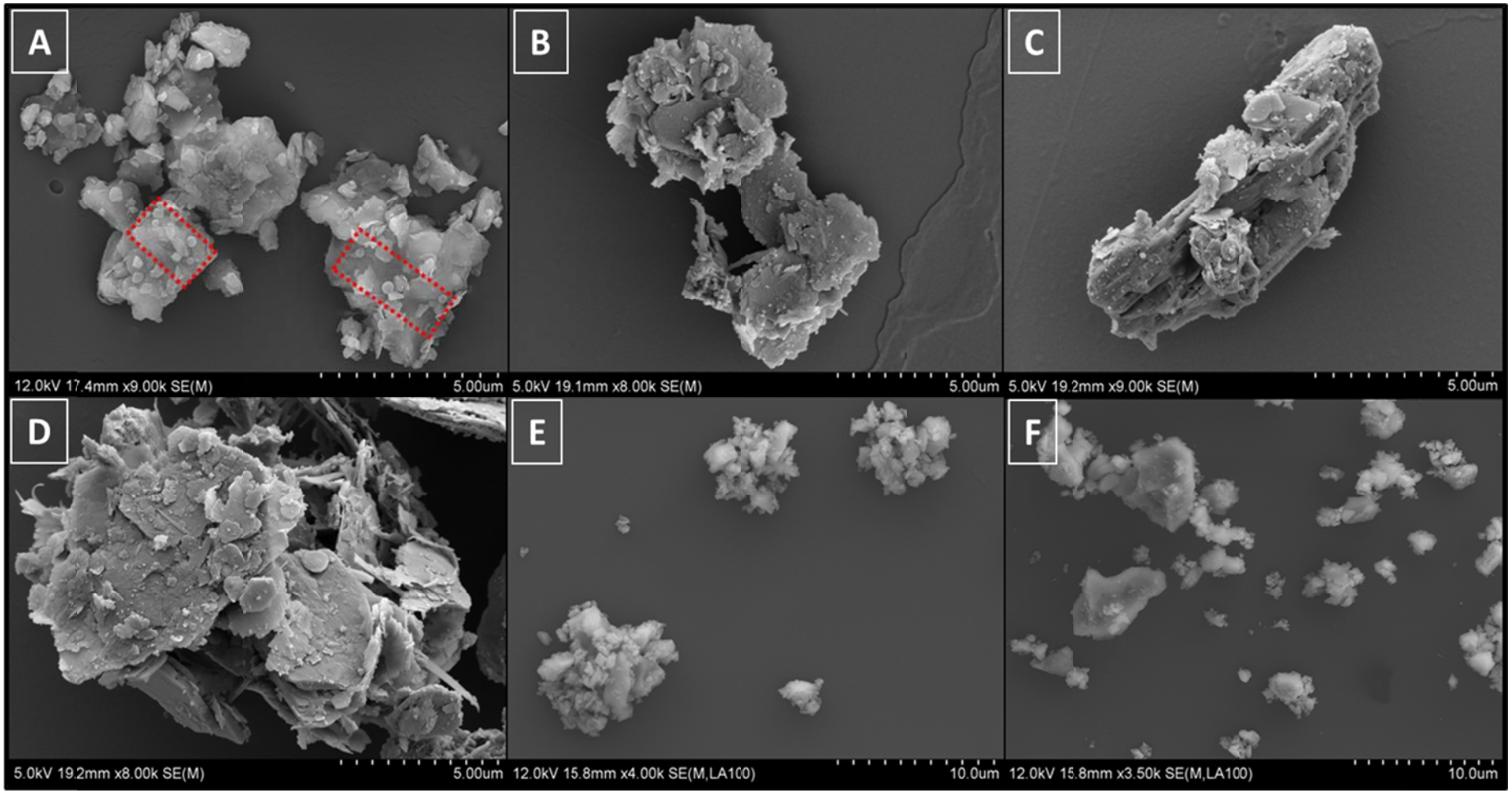


Figure 4.15 Representative SEM images of typically observed morphologies in the respirable fraction of non-volcanic quarry dusts. A – greywacke; B-D – raw sandstone; E and F – sandstone processed into cristobalite. Red boxes show particles with spherical morphology.

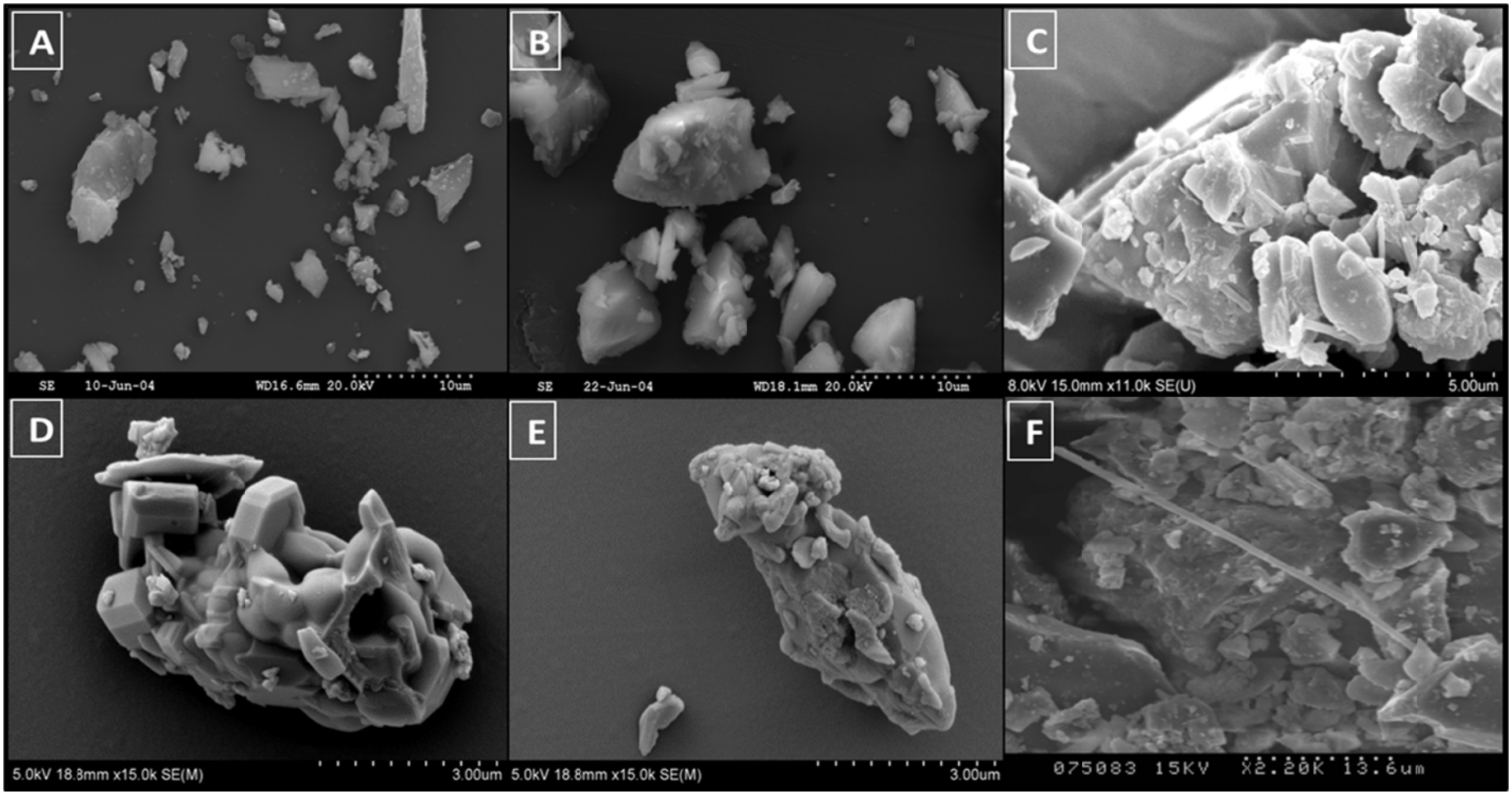


Figure 4.16 SEM images of the respirable fraction of ash samples from: A – Cerro Negro (imaged by C. Horwell); B – Etna (imaged by C. Horwell); C – Eyjafjallajökull (imaged by D. Damby); D and E – Soufrière Hills (imaged by author) E showing fused mineral grains; F – Chaitén (imaged by J. Le Blond) showing fibre-like particle confirmed as gypsum [5].

4.4.4.2 Thin section and resin stub morphologies

Thin sections were taken of samples which contained >10 wt.% crystalline silica (total of all three polymorphs), which occurred in samples from Montserrat and in the obsidian from New Zealand (see Section 4.4.4) in order to investigate the purity of crystalline silica present and to determine whether there were any adhering minerals or surface occlusion.

Spherulites were observed in the thin sections of obsidian rock from Henderson quarry, by J. Close, making up the bulk of some dome rock samples (e.g. Obs_05, forming up to 90% of the rock mass (excluding pore spaces)(Close, 2012)). These are abundant and measure up to ~4 mm, also including occasional phenocrysts. Spherulites are often centred on vesicles (seen in lower left of Figure 4.17), are rarely complete, and have characteristic colour banding (Close, 2012). The spherulites are assumed to be composed of interlocking crystals of cristobalite and potassium feldspar, except around vesicles where large tridymite crystals (up to 1 mm) can be observed growing into the pore space (as can be seen in Figure 4.17) typically as 'arrow-head' shaped crystals.

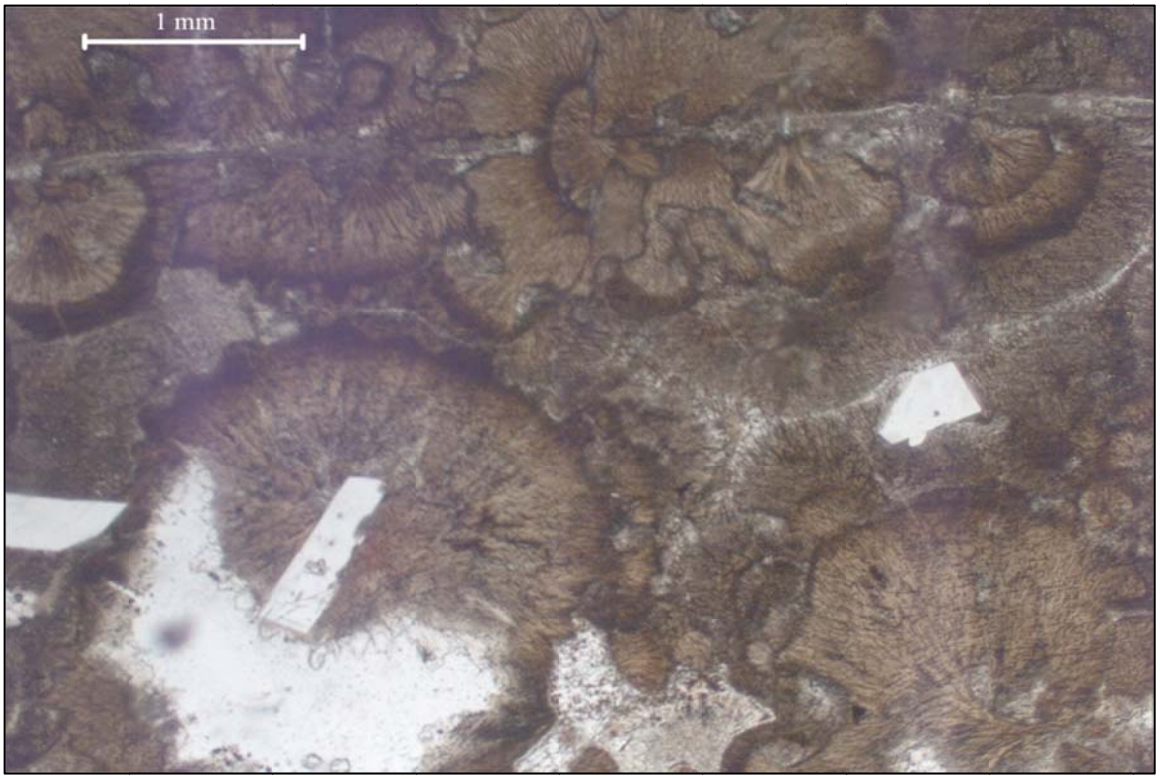


Figure 4.17 Light microscope image of spherulites from a whole rock sample of obsidian (Henderson Quarry, New Zealand) Imaged by J. Close.

Particles comparable to typical dome collapse volcanic ash were observed in the polished sections of dust samples from the Montserrat quarries (Belham Valley, Trants and, to a much lesser extent, Little Bay). A particle from Little Bay, Montserrat (from the Silver Hills deposit) is shown in Figure 4.18 which is quite different from most quarry dust or volcanic ash derived from the Soufrière Hills volcano. The image shows the glassy matrix is almost entirely missing with void space surrounding the microlites. This is not unusual for highly devitrified dome rock (Horwell *et al.*, 2013b), however, areas of fibre-like, feathery textures can also be seen in the particle (examples are shown in Figures 4.19- 4.20), where it is likely that feldspars have weathered over time to clay minerals. This is highlighted further in Figure 4.19 which shows a magnified area of the feathery texture highlighted in red near Spectrum 2 of Figure 4.18; the EDS patterns for these data indicate the level of Al is similar to Si. For clays, one would expect the Al and Si peaks to be of similar height (as demonstrated in the Soufrière Hills ash by (Horwell *et al.*, 2003b)). Other analyses of these textures also show this characteristic EDS spectra.

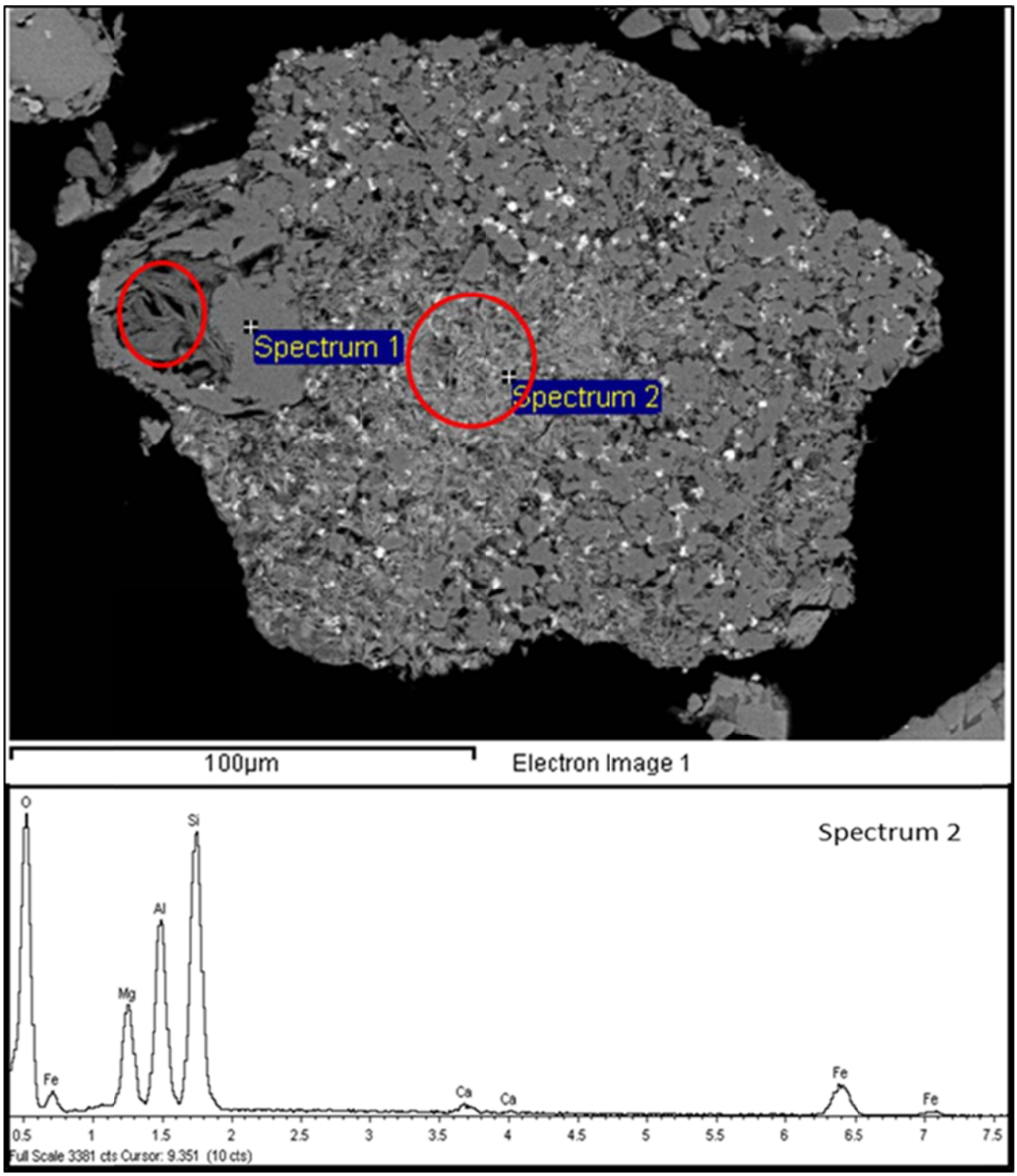


Figure 4.18 An SEM image of a dust particle in thin section, similar to devitrified dome rock, with feathery texture in the centre and to the left (indicated in red circles), from Little Bay (Montserrat). The area within the circle near spectrum 2 is shown in greater magnification in Figure 4.19.

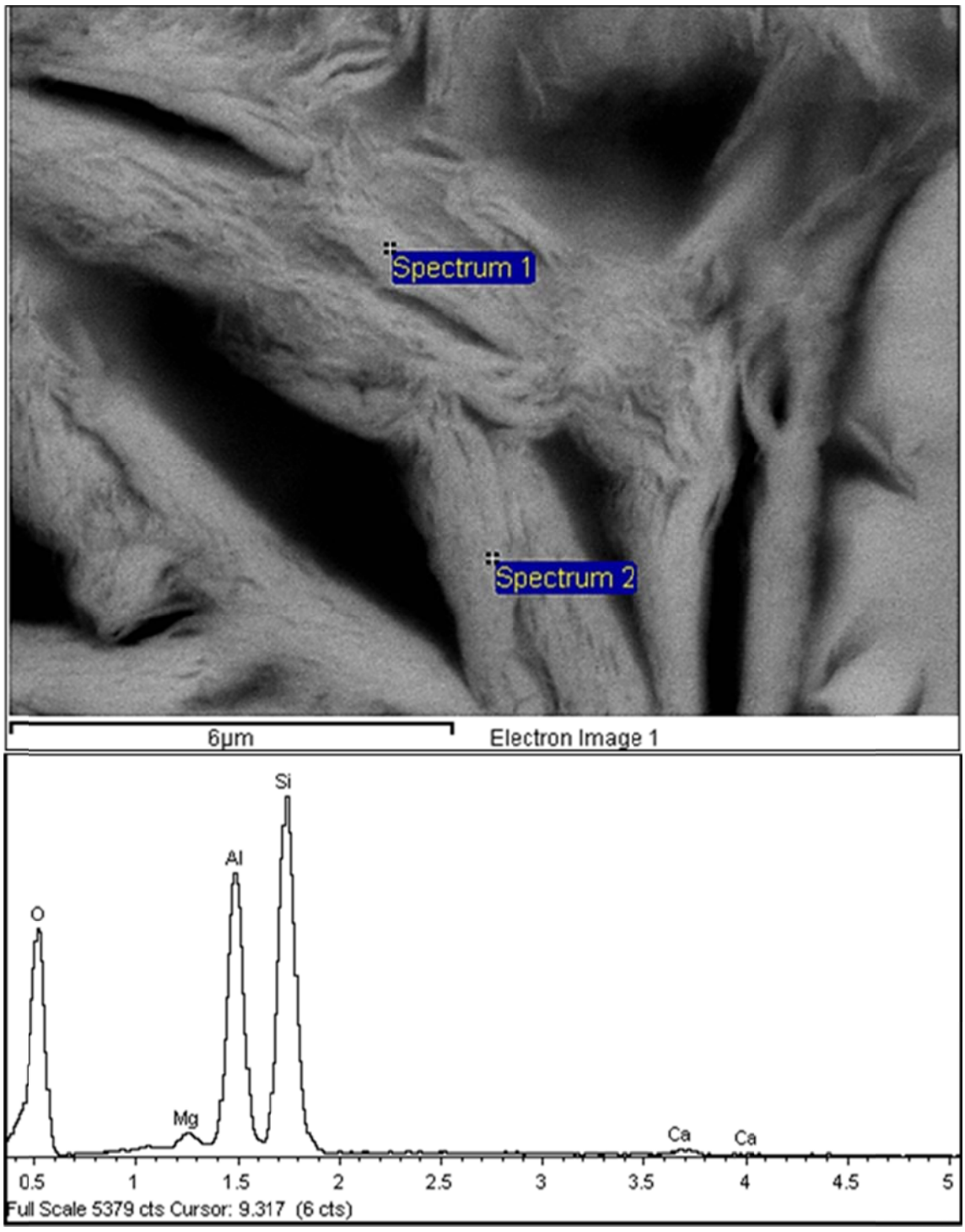


Figure 4.19 A high-resolution SEM image of the feathery texture near spectrum 2 of Figure 4.25 shown, with a characteristic EDS spectrum for clay.

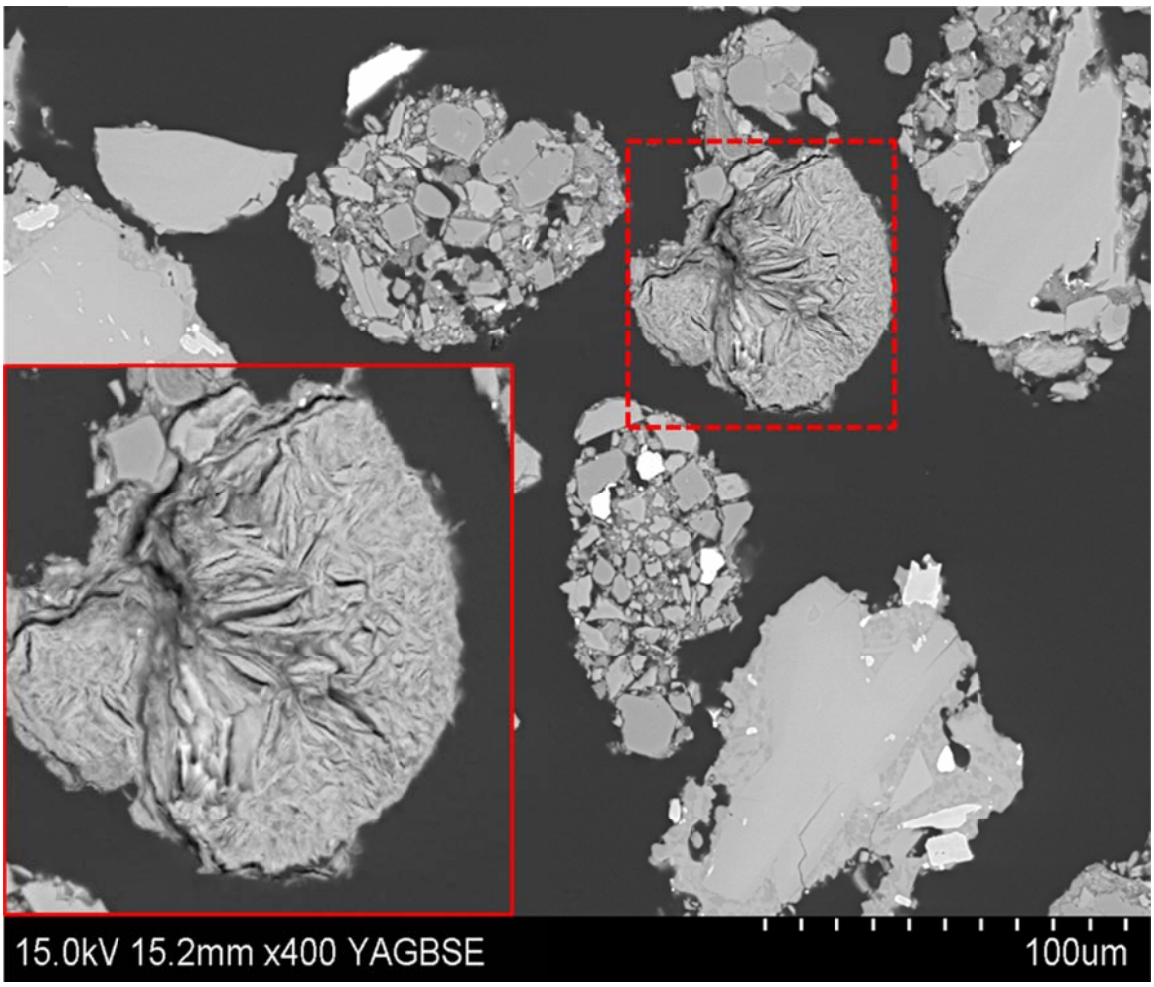


Figure 4.20 Typical dust particles from Little Bay, with one particle showing feathery, fibre-like textures, shown to have the EDS spectrum for clay (inset: highlighted area magnified).

4.4.4.3 Surface occlusion of silica

Particles from quarries across Montserrat rarely appear composed of single crystals. They are most often observed as aggregates of minerals within single particles. Figure 4.21 shows three large particles at increasing magnification which show dark grey, hexagonal to sub-hedral patches amongst lighter grey lath-shaped crystals. This was most commonly observed in larger particles (inhalable but not respirable) in dust samples which originated from Little Bay, where ancient deposits are being quarried. Following petrological work of Soufrière Hills dome rock and ash by (Horwell *et al.*, 2013b), the mineralogy of the particles can be interpreted from SEM observations and EDS analyses (Horwell *et al.*, Post review). Crystalline silica appears dark grey, with feldspar and

volcanic glass being lighter shades of grey. Cristobalite is recognised by characteristic 'fish-scale' cracking whereas quartz, formed by devitrification, is often hexagonal to sub-hedral and is not cracked. Feldspar is usually lath shaped.

In Figure 4.21, compositions of the dark grey, hexagonal crystals were confirmed to contain only SiO_2, and their morphology concurred with that observed by Horwell et al. 2013, so they are interpreted as quartz formed during total devitrification of the glassy groundmass. In some grains, the quartz and cristobalite was not only surrounded by feldspar but also the feathery clay minerals identified above. Figure 4.22 shows cristobalite grains (based on their greyscale and EDS compositions (high Si) indicated by spectra 1 and 4. These are embedded in a phyllosilicate matrix (high Si and Al, with Mg, Ca and Fe) indicated by spectra 2 and 3.

It can clearly be seen from these polished block images, that crystalline silica typically has its surfaces coated by surrounding minerals and that, for the ancient Little Bay samples (Silver Hills Complex), clay minerals are also present.

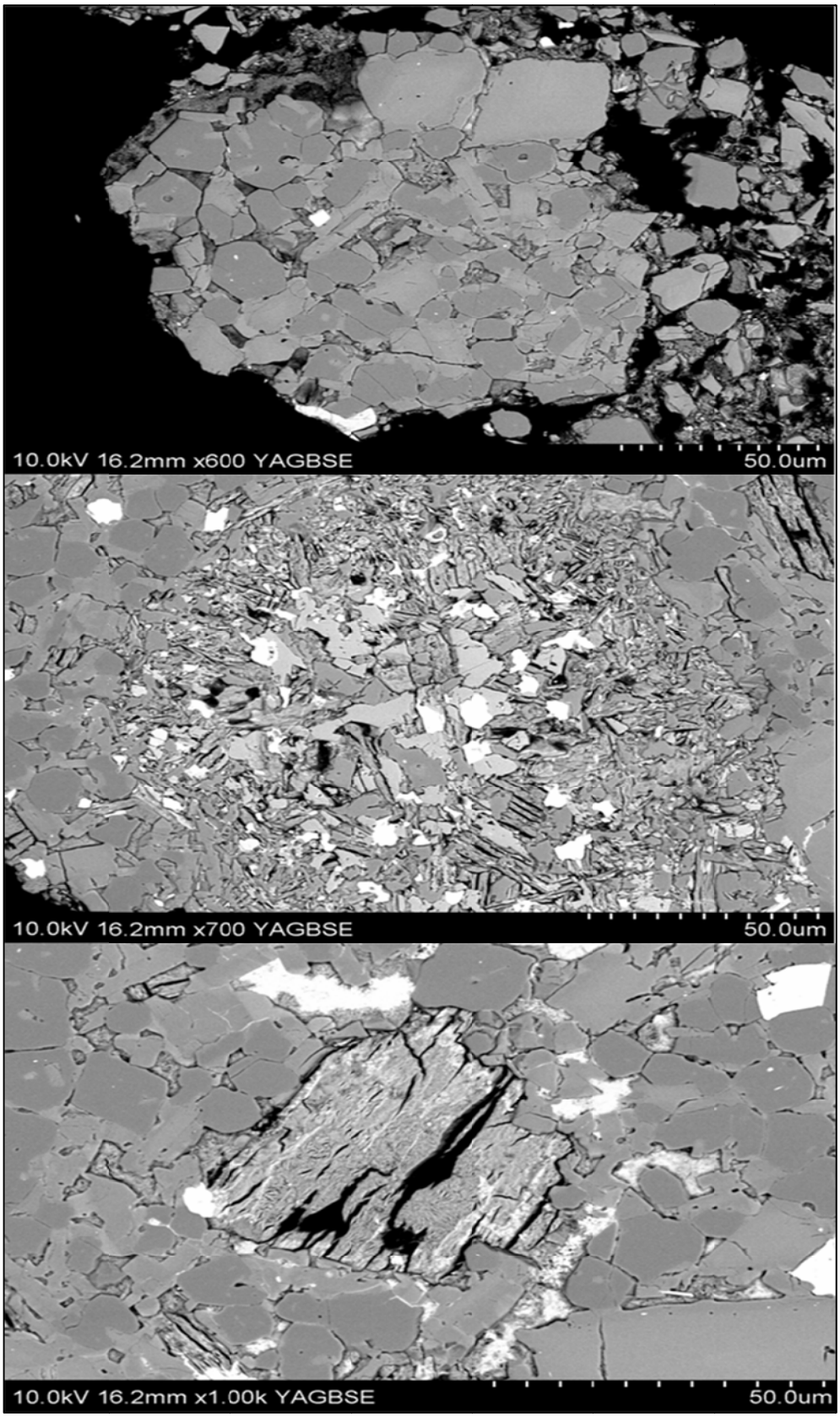
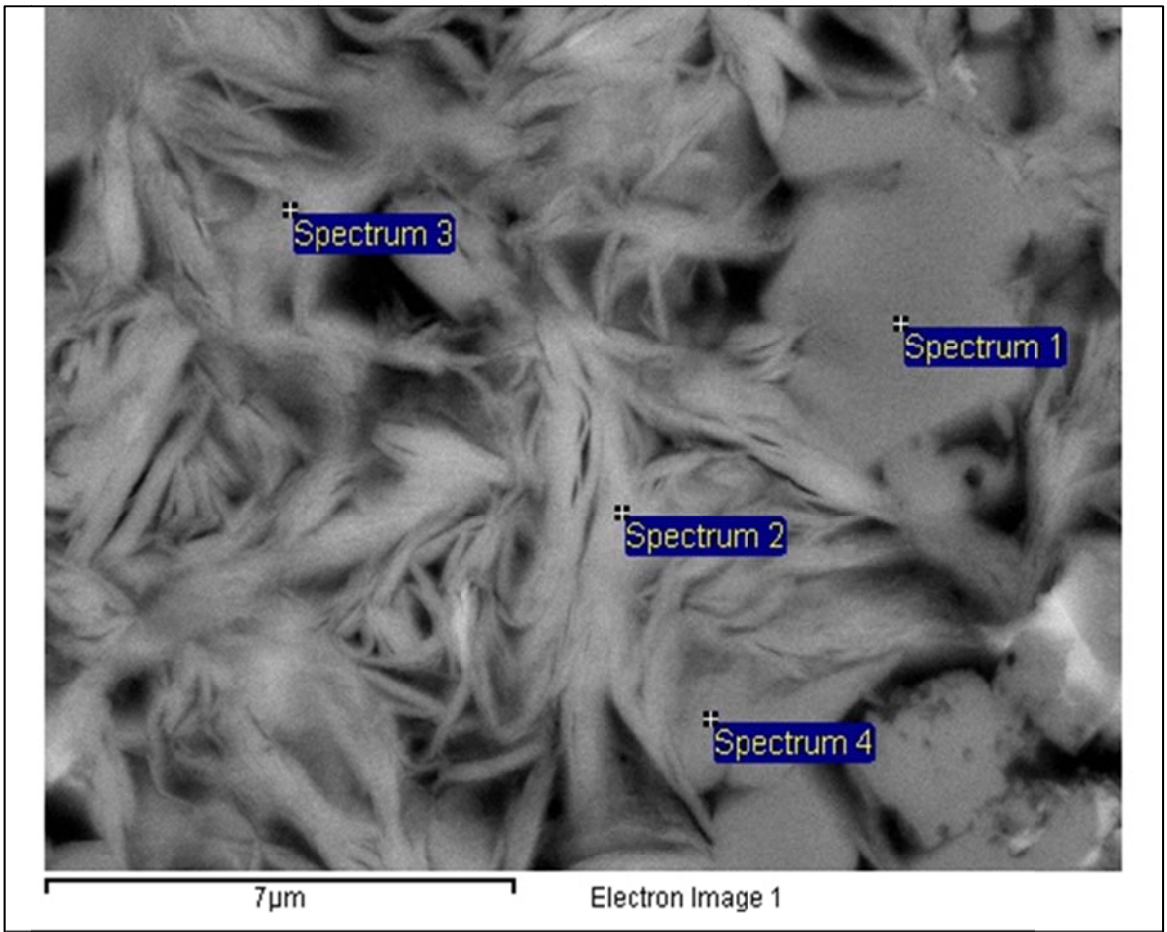


Figure 4.21 A large particle with degrading groundmass and areas of in-filled altered minerals. The darker grey hexagonal minerals are likely to be quartz and typically appear surrounded by feldspar or volcanic glass (lighter grey), or clay (phyllosilicate) minerals (feathery texture).



PH_02	Na	Al	Si	Ca	Total
Spectrum 1	-0.02	0.95	98.99	0.07	100.00
Spectrum 3	1.21	31.79	65.76	1.24	100.00
Spectrum 4	0.11	1.99	97.90	0.01	100.00

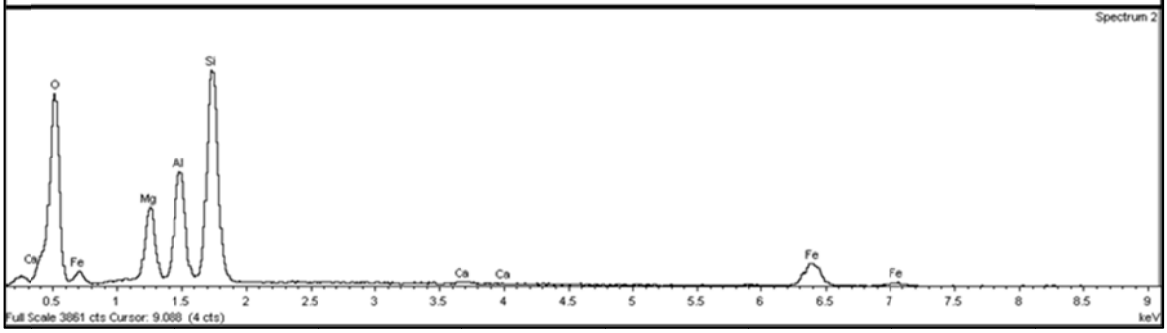


Figure 4.22 Section of a particle which shows cristobalite grains (spectra 1 and 4) surrounded by phyllosilicates (feathery textures, spectra 2 and 3) with elemental composition of spectra in oxide wt. %. Spectrum two is presented graphically.

4.4.5 Crystalline Silica Quantification

The crystalline silica content was investigated for a range of samples, to semi-quantitatively determine the presence of the polymorphs quartz, cristobalite and tridymite. Mafic samples were investigated as tholeiitic basalts can contain a few wt.% quartz; however, the majority of samples investigated were intermediate and felsic ones which contain more SiO_2 than mafic samples. Around half the samples were run once, however, those samples which yielded higher levels of crystalline silica (notably from the andesitic quarries on Montserrat) were repeated (the data for each individual run are contained in Appendix II). Figure 4.23 shows an example of the patterns obtained for samples containing both quartz and cristobalite, whilst Figure 4.24 shows a sample which contained tridymite. The averaged results (N=2) are presented in Table 4.12.

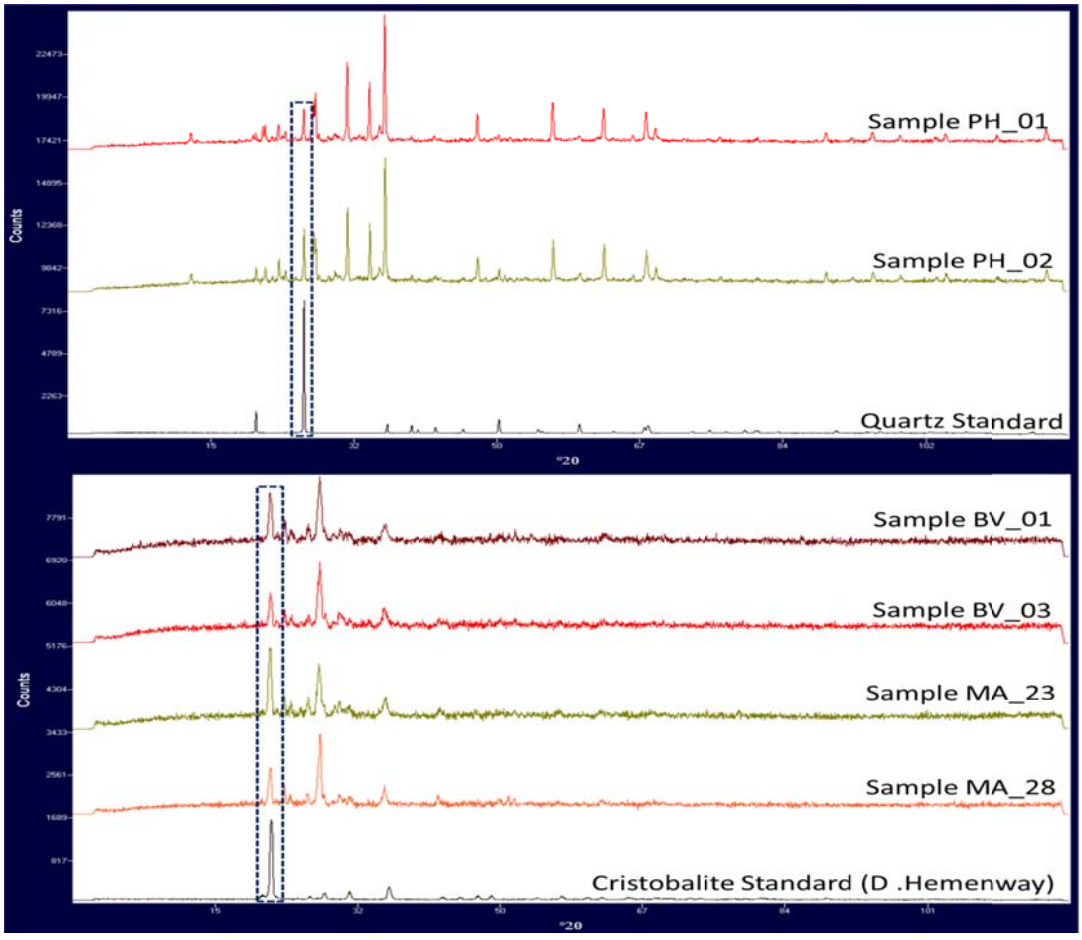


Figure 4.23 XRD patterns from Montserrat samples of quarry dust (PH_01, PH_02, BV_01, BV_03) and volcanic ash (MA_23, MA_28) along with the standards for quartz and cristobalite with the area of their main peaks indicated.

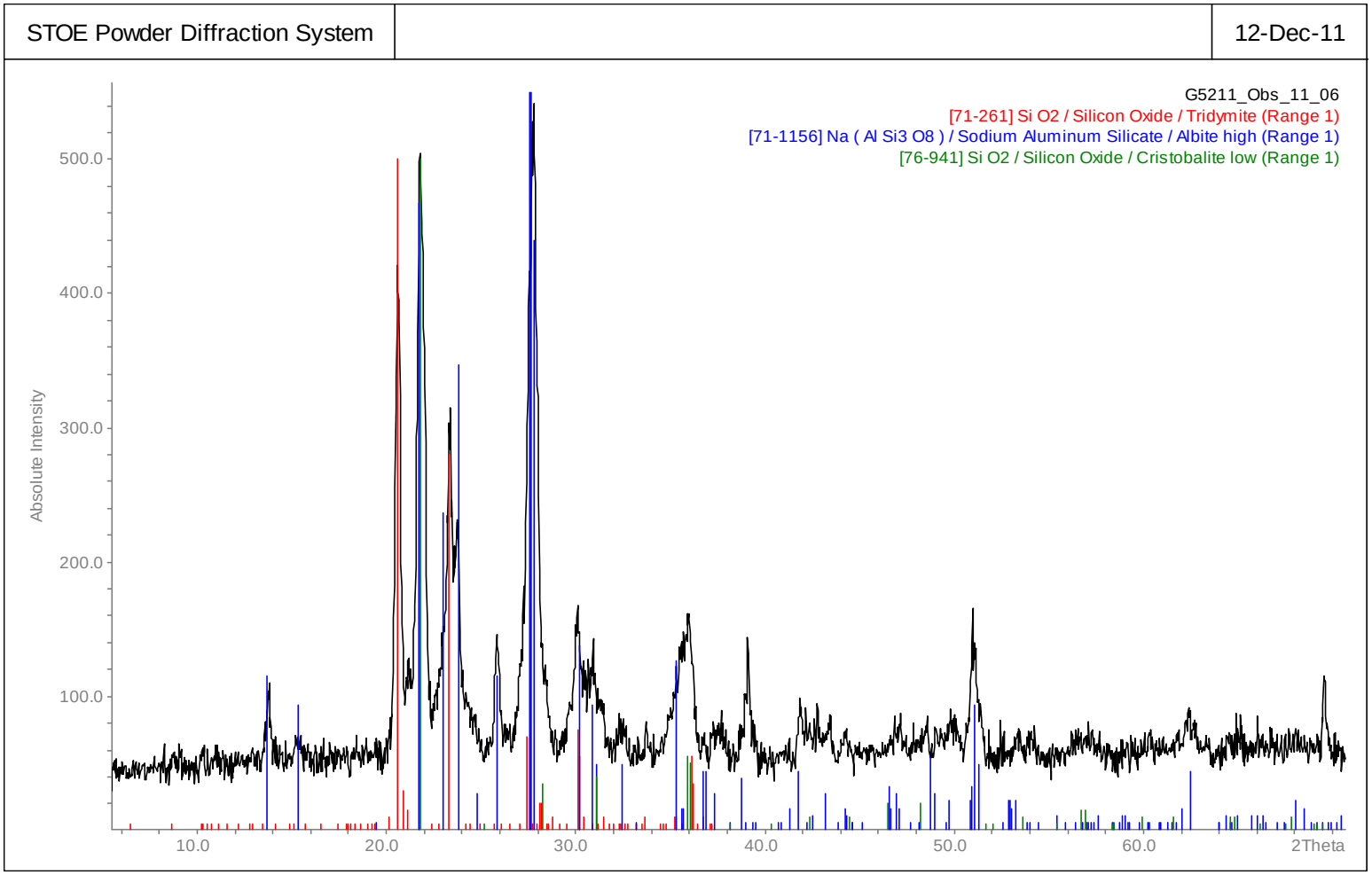


Figure 4.24 XRD patterns for a sample of Obsidian from Henderson's quarry (in black) and standard for tridymite (in red)

Table 4.12 The semi-quantitative detection of the three crystalline silica polymorphs in quarried volcanic samples, volcanic ash and non-volcanic quarried samples. Samples containing >10 wt.% total crystalline silica are indicated with grey shading. ND = Not detected. [+](Close, 2012) *(Horwell *et al.*, 2013a) [§](Horwell *et al.*, 2008).

Magma Type	Sample	Cristobalite (wt. %)	Quartz (wt. %)	Tridymite (wt. %)	Total Crystalline Silica Content (wt. %)
Mafic quarry dust	FT_01	ND	1.0	ND	1.0
	FT_03	ND	1.0	ND	1.0
	P2_01	ND	ND	ND	0.0
	P2_05	ND	ND	ND	0.0
	BY_01	ND	ND	ND	0.0
	BY_02	ND	ND	ND	0.0
Intermediate quarry dust	PH_01	2.5	16.0	ND	18.5
	PH_02	2.0	16.0	ND	18.0
	BF_01	10.0	5.0	ND	15.0
	BV_01	12.0	2.0	ND	14.0
	ED_02	10.0	4.0	ND	14.0
	BV_02	11.0	2.0	ND	13.0
	ED_01	9.0	2.0	ND	11.0
	BV_03	8.0	1.0	ND	9.0
	BV_04	5.0	1.0	ND	6.0
Felsic quarry dust	Obs_01[+]	11.0	ND	18.0	29.0
	Obs_02[+]	8.0	ND	10.0	18.0
	Obs_03[+]	6.0	ND	12.0	18.0
	TP_04	1.5	6.0	ND	7.5
	Obs_04[+]	7.0	0.0	ND	7.0
	TP_05	1.0	3.0	ND	4.0
	AT_04	1.0	1.0	ND	2.0
	LA_04	1.0	1.0	ND	2.0
	LA_02	1.0	1.0	ND	2.0
	AP_02	ND	2.0	ND	2.0
	AP_01	ND	1.0	ND	1.0
Mafic volcanic ash	EY_13*	2.0	1.0	ND	3.0
	Fuego	ND	1.0	ND	1.0
	V1872	ND	ND	ND	0.0
	V1906	ND	ND	ND	0.0
Intermediate volcanic ash	SHV_1999[§]	15.0	1.0	ND	16.0
	SHV_2003[§]	12.0	2.0	ND	14.0
Felsic volcanic ash	Chai_10[§]	19.0	2.0	ND	21.0
	Chai_11[§]	17.0	1.0	ND	18.0
	Chai_09[§]	14.0	1.0	ND	15.0
	Chai_02[§]	7.0	2.0	ND	9.0
Greywacke	HU_03	ND	14.0	ND	14.0
	HU_04	ND	18.0	ND	18.0
Sandstone	MS_Crist	99.0	1.0	ND	100.0
	MS_Raw	0.0	98.0	ND	98.0

The majority of mafic samples of both quarry dust and volcanic ash, contain very little crystalline silica 0-3 wt.%. Basaltic samples from Flat Top Quarry (FT01, FT03) contain a total of 3 wt.% crystalline silica, likely due to silica over-saturation (this sample lies on the tholeiitic basalt boundary as shown in Figure 4.3). The majority of rhyolitic samples also contain low amounts of crystalline silica, aside from a pumice sample from Te Puke (7.5 wt.% quartz) and the samples of obsidian from Henderson analysed by Jon Close which contain elevated levels of cristobalite and tridymite (Close, 2012). Obs_01, a dust sample from the collection area at Henderson's Quarry, where an obsidian lava dome is quarried, is composed of 29 wt.% crystalline silica. Samples of Chaitén ash (erupted from collapse of an obsidian lava dome) also contain high levels (15-21 wt.%) of cristobalite, except for sample Chai_02 which was from an earlier (explosive) phase of the eruption. Felsic magmas contain high levels of SiO_2, however, in the majority of pumice samples presented here, those which contained very little crystalline silica are almost entirely amorphous, as shown in XRD patterns in Figure 4.25.

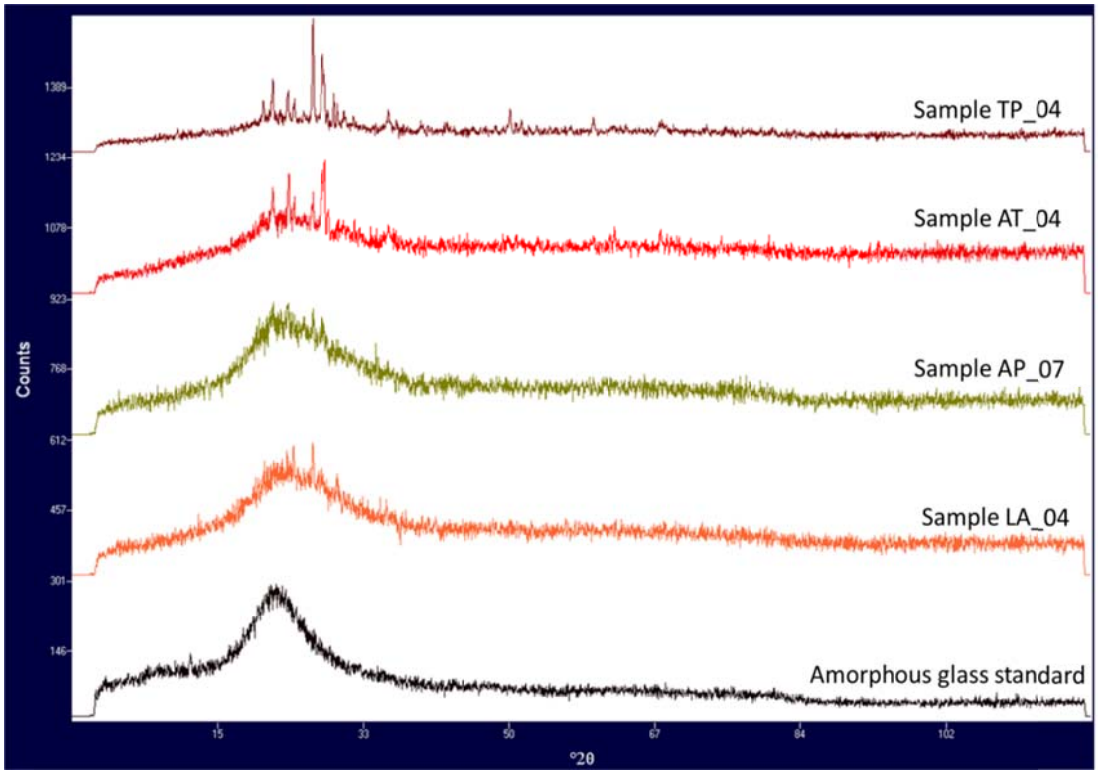


Figure 4.25 XRD patterns from a range of felsic samples, including two which contained a few wt.% crystalline silica (TP_04, AT_04 from New Zealand) and those which contained only ~1 wt. % (AP_07, LA_04 from Yali) in comparison to a standard of amorphous glass with the characteristic 'hump' in place of distinct peaks.

The quarried samples from Trants and the Belham Valley, Montserrat, contain similar proportions of cristobalite (9-12 wt. %) to the ash samples from the dome collapse events at the Soufrière Hills volcano in Montserrat (12-15 wt. %) (Horwell *et al.*, 2014, Horwell *et al.*, 2013b). Two samples from Little Bay (quarrying the Silver Hills complex), contain substantial amounts of quartz and very little cristobalite.

The non-volcanic greywacke (from Hunua, New Zealand) and sandstone (Moneystone, UK) contain the most crystalline silica, with 14-18 wt. % and up to 100 wt. % respectively. At Moneystone quarry, sandstone rich in near-pure quartz is quarried and processed to produce pure cristobalite (the processing involves crushing, acid leaching and high temperature heating in a kiln) for commercial applications. Figure 4.26 shows the transition from quartz to cristobalite, before processing (MS_Raw) and as finished product (MS_Crist).

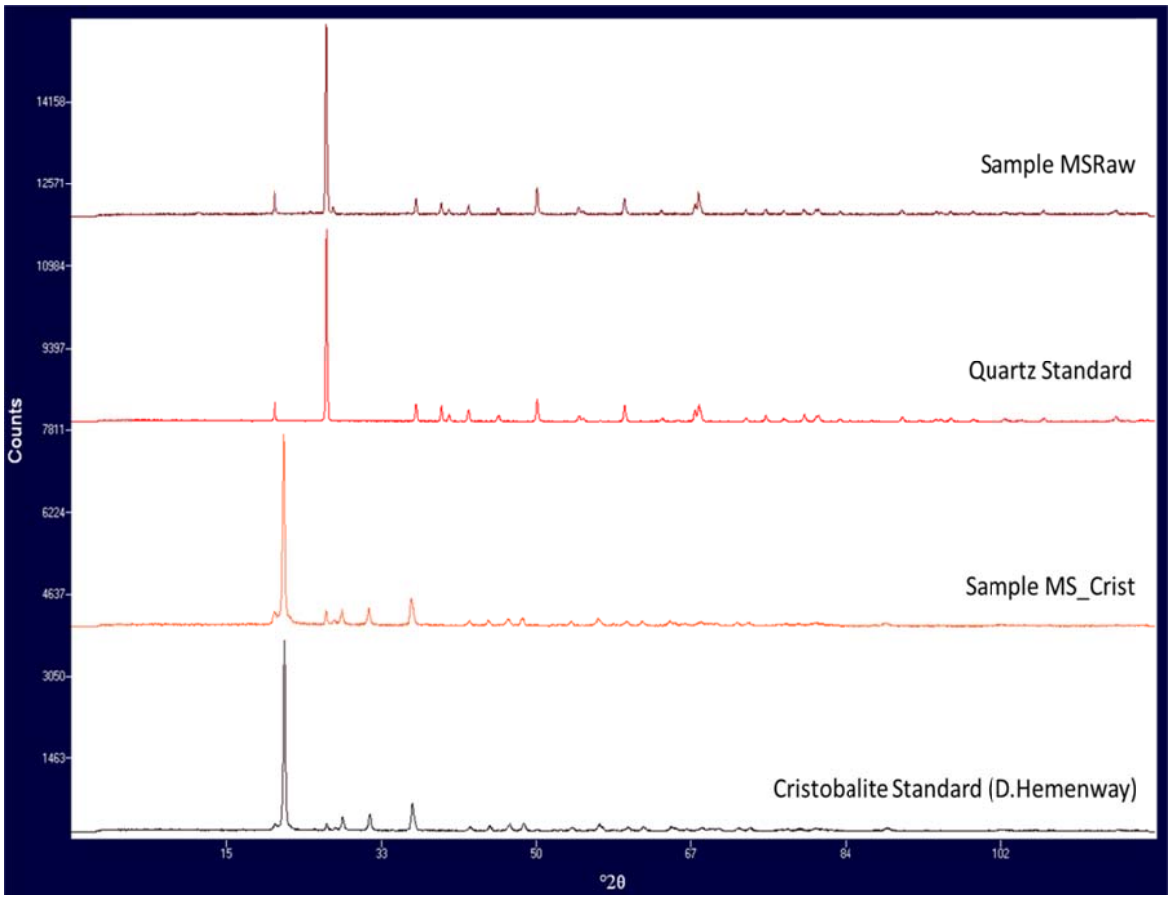


Figure 4.26 XRD patterns for raw material from Moneystone quarry with a quartz standard for comparison (upper two patterns) and the post-processing finished product with a cristobalite standard for comparison (lower two patterns).

The average total cristobalite content of quarry dust and volcanic ash, by location/eruption, of intermediate and felsic composition is shown in Figure 4.27, grouped by mode of emplacement. For the intermediate samples, the ancient PDCs contain the least cristobalite on average (2.5 wt.%) whilst the modern PDCs contain substantially more (9-9.6 wt.% average at Trants and the Belham Valley, respectively) and the ash from dome collapse events contains the most at 13.5 wt.%. For the felsic deposits, the air fall pumice contained 1-1.5 wt.% (for Lava and Te Puke respectively) whilst the hydrated obsidian (perlite) contained none. The Chaitén explosive ash (from the early stages of the eruption) contained 7 wt.% whilst the ash from dome-collapse contained 16.7 wt% (from the later stages of the eruption, following dome growth).

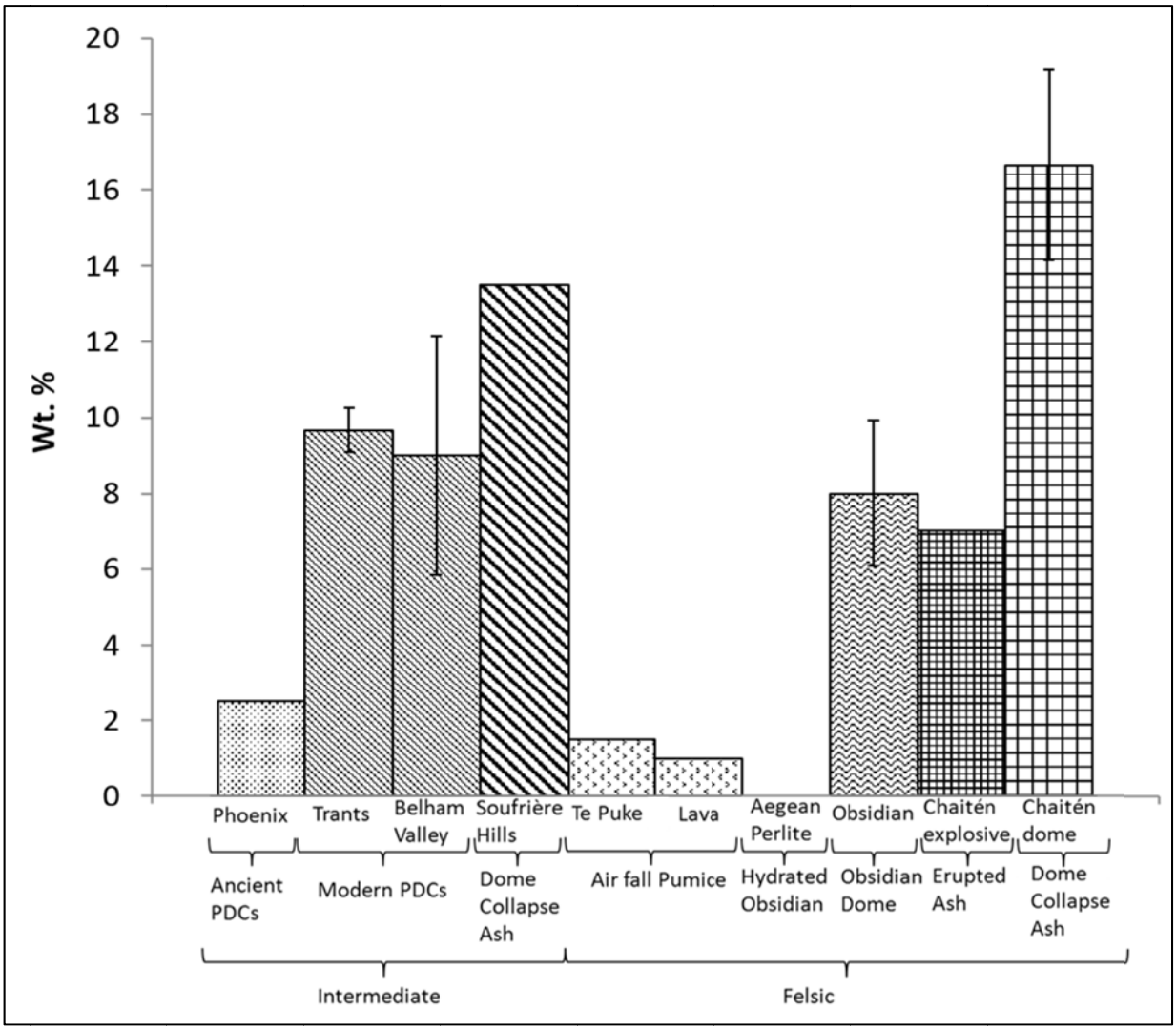


Figure 4.27 Average cristobalite content for different quarries and volcanic ash samples of intermediate and felsic composition. Error shown is 1σ for samples where n=≥3.

4.5 Results ≤10 µm Fraction

4.5.1 Grain size analysis

The grain size distribution of the separated fraction was analysed using a Beckman-Coulter LS230 Laser Diffraction Particle Size Analyzer with PIDS (Polarization Intensity Differential Scattering), in order to confirm that the majority of the material was of a PM10 fraction. The results are presented in Figure 4.28 and indicate that all samples contained 82-98 cu.vol.% <10 µm and 100 cu.vol% of ≤15 µm which indicates successful separation of a lung pertinent fraction from the sieved <1mm 'bulk' fraction (note that for larger size fractions there is less comparability with the Malvern Mastersizer data).

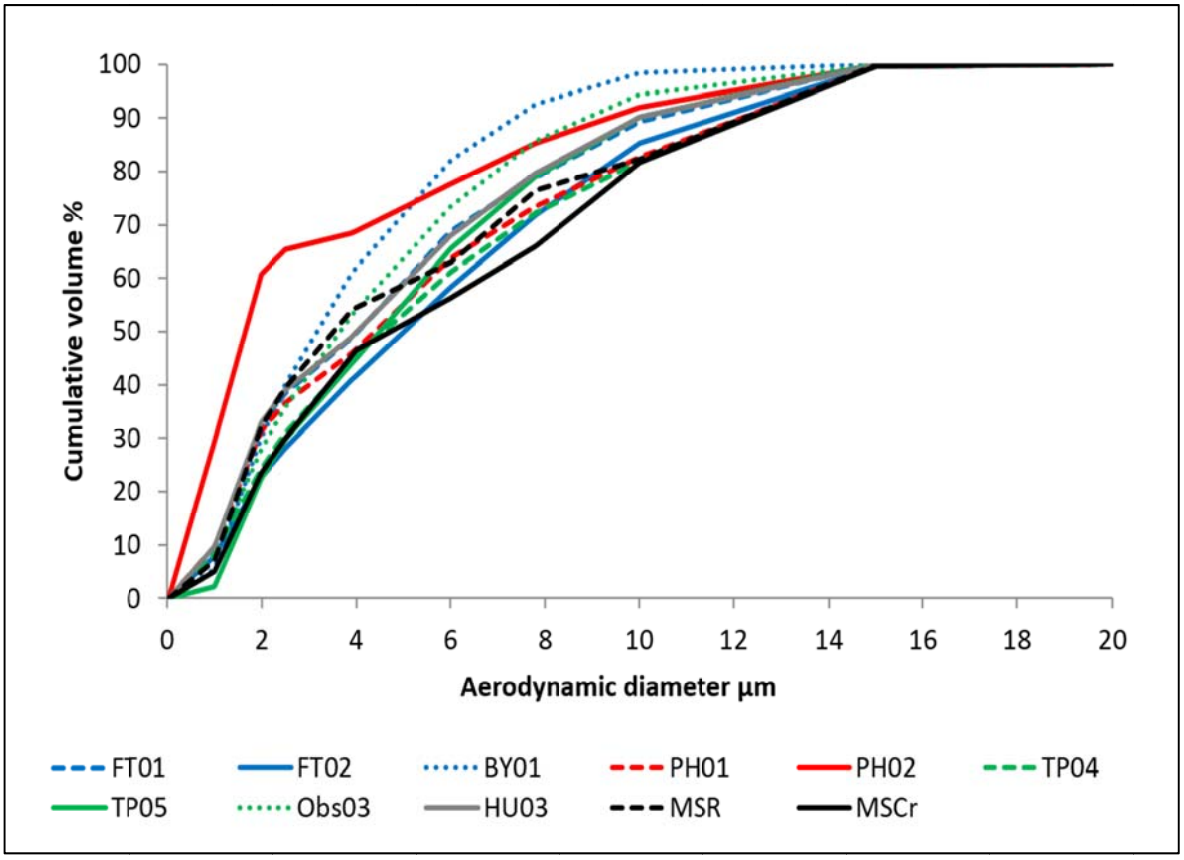


Figure 4.28 Aerodynamic diameter of the tumbler-separated fraction as reported by a) Beckman-Coulter and b) adjusted for the Malvern Mastersizer. Green – mafic; red – intermediate; blue – felsic; purple – greywacke; brown – sandstone.

4.5.2 Particle Morphology

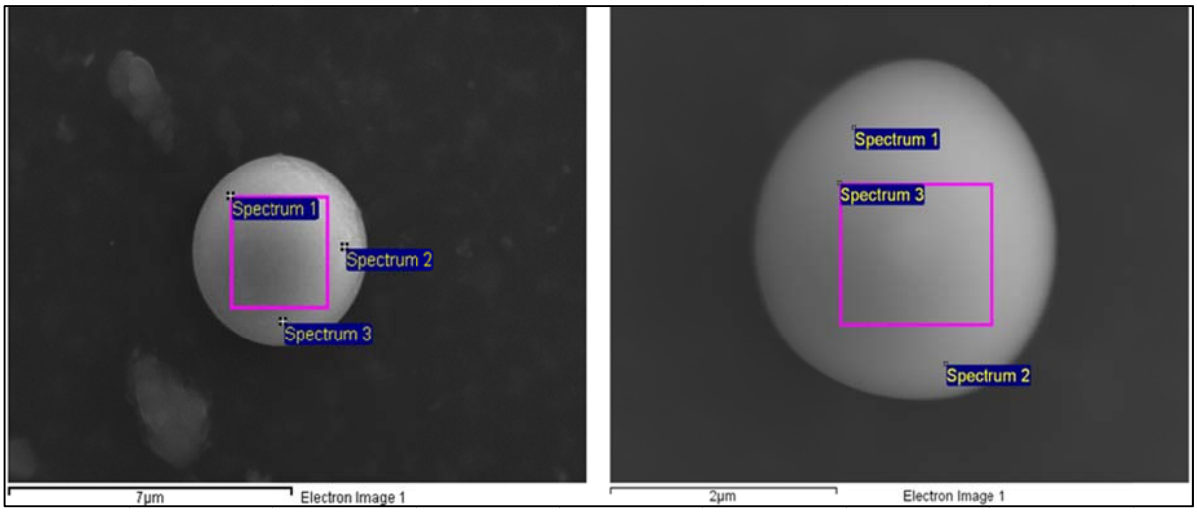
The aspect ratio (shape factor) which ranges from 0 for elongate (fibre-like) particles to 1 for equiaxed particles was measured for <10 µm particles from 11 quarried samples. Over one thousand particles were analysed for each sample and the average aspect ratio calculated; the results are presented in Table 4.13. The results show broad similarities in aspect ratio across all sample types. Overall they are towards the equiaxed end of the spectrum with a range of 0.59-0.70. The 2σ error lies between 30 and 60% of the mean for six samples, but between about 70 and 85% for the remaining five (Table 4.10). The large values reflect the fact that there was substantial variability within the samples; however no fibre-like samples were observed.

Table 4.13 The aspect ratio of quarry dusts, with error to 2σ (n=1000-1250)

Type	Sample	Aspect Ratio	2σ	2σ/Average
Mafic	BY01	**0.70**	**0.35**	**0.50**
	FT01	**0.68**	**0.36**	**0.53**
	FT02	**0.59**	**0.50**	**0.85**
Intermediate	PH01	**0.59**	**0.32**	**0.54**
	PH02	**0.60**	**0.48**	**0.80**
Felsic	TP04	**0.67**	**0.21**	**0.31**
	TP05	**0.69**	**0.29**	**0.42**
	Obs03	**0.65**	**0.48**	**0.74**
Greywacke	HU03	**0.60**	**0.45**	**0.75**
Sandstone	MSRaw	**0.68**	**0.40**	**0.59**
	MSCr	**0.62**	**0.43**	**0.69**

Specific particles of interest, e.g. fibre-like or spherical particles were also analysed by EDS. Spherical particles are of interest because they are particularly aerodynamic and can penetrate deep into the lungs (Crowder *et al.*, 2002). Spheres of Si, O composition (by EDS) occur occasionally within samples, being present in many of the samples from the intermediate and felsic groups, but rarely in the mafic dusts. The spheres are often purely composed of silica and oxygen, as shown in figure 4.29, but occasionally contained additional elements such as sodium and aluminium, indicating that

they could be cristobalite (Horwell et. al. (2013b). Soufrière Hills cristobalite generally contains up to 4 wt. % Al and Na in its structure, whereas quartz is almost pure SiO_2 (Horwell *et al.*, 2013b). Despite the spheres being present in Montserrat deposits, they have not been identified by previous workers in the ash deposits. Spheres have been observed in volcanic plumes from Kilauea, Hawaii (Hon & Orr, 2011, Meeker & Hinkley, 1993), which are also <5µm in diameter (Hon & Orr, 2011) and composed of spinel in one eruption (early 1990s)(Meeker & Hinkley, 1993) and more recently composed of hexahydrite (2008-2010)(Hon & Orr, 2011). Spheres have also been observed in the plume from Etna composed of glassy silicates (Lefevre *et al.*, 1986) and in the cinder cone of Cabezo Segura (Spain) (Carracedo Sanchez *et al.*, 2009).



JN_01	Na	Al	Si	Ca	Total	BV_02	Na	Al	Si	Ca	Total
Spec. 1	3.07	0.90	96.07	-0.03	100	Spec. 1	0.61	0.14	99.25	-0.01	100
Spec. 2	3.37	4.99	91.53	0.11	100	Spec. 2	0.06	0.08	99.65	0.20	100
Spec. 3	2.03	1.07	96.78	0.12	100	Spec. 3	-0.03	0.08	99.93	0.02	100

Figure 4.29 Spheres of SiO_2 from dust from Trants (left, JN_01) and the Belham Valley (right, BV_02), both from Montserrat, with their elemental composition shown below as oxide compound %.

4.5.3 Crystalline Silica Content

The crystalline silica content was investigated for the <10µm separated samples, to semi-quantitatively determine the presence of the crystalline silica polymorphs; previous analysis on dome collapse ash from the Soufrière Hills volcano has found enrichment of the <2 µm fraction in ash from the lofting co-PDC plume in comparison to the PDC matrix (due to mineral fractionation) (Horwell *et al.*, 2003b). Some of the quarried modern PDC samples in this study may contain material from dome-collapse events, therefore there is potential for a difference in the crystalline silica content of the <1mm bulk fraction compared to the ≤10 µm separated fraction.

There was, however, very little difference observed between the <1mm fraction (Table 4.12) and the ≤10 µm separated fraction shown in Table 4.14. The results general fall within the 3 wt. % margin of error, except for the samples from Phoenix quarry (PH01, PH02) which contain substantially more crystalline silica in the ≤10 µm fraction, ~28 wt.% total compared with ~18 wt. % in the <1mm fraction; it should be noted, however, that the error associated with peak integration is larger where there is a greater quantity of the phase of interest and therefore repeated measurements should be taken (these were not possible here due to scarcity of sample). Furthermore, due to sample scarcity only one analysis was run so these results should be viewed only as indicative.

Table 4.14 The crystalline silica content of ≤10 µm fraction (n=1) and the <1mm fraction (n=2) in wt.% ND: none detected.

Magma Type	Sample	Cristobalite		Quartz		Tridymite		Total Crystalline Silica Content	
		≤10µm	<1mm	≤10µm	<1mm	≤10µm	<1mm	≤10µm	<1mm
Mafic	FT01	ND	ND	1.3	1.0	ND	ND	1.3	1.0
	FT02	ND		1.4		ND		1.4	
Intermed-iate	PH01	3.7	2.5	25.3	16.0	ND	ND	29.0	18.5
	PH02	4.0	2.0	23.2	16.0	ND	ND	27.2	18.0
Felsic	TP04	3.0	1.5	8.0	6.0	ND	ND	11.0	7.5
	OBS03	4.0	6.0	ND	ND	14	12	18.0	18.0
Non-volcanic	HU03	0.0	ND	15.0	14.0	ND	ND	15.0	14.0
	MSRaw	0.0	0.0	98.0	98.0	ND	ND	98.0	98.0
	MSCr	98.0	99.0	1.0	1.0	ND	ND	99.0	98.0

4.6 Discussion

The aim of this study is to assess the physical characteristics of volcanic quarry dusts, which may control the potential toxicity of the particles in the lung. An extensive sample set was collected, spanning several magma types and representing a wide range of eruption styles and deposits. The suite of analyses conducted provides data from which to unpick relationships between characteristics which, in turn, will be related to the specific deposit types and dust generating activities in the quarries, as well as to volcanic ash which could potentially be used as a proxy for hazard assessment.

4.6.1 Appraisal of hypotheses and comparison of health-relevant parameters

1) *The proportion of thoracic (<10µm) and respirable (<4µm) material within volcanic quarry dust differs depending on which stage of the quarrying process it is produced at; e.g. raw material, processed, finished product.*

The energy level associated with the mode of fragmentation of quarried material is dependent on the deposit type with lava flows or domes requiring high-energy extraction associated with the generation of finer dust, whilst friable deposits require little energy for extraction and processing (Bohloli and Hoven, 2007; Guimaraes et al., 2007); however, their grain size is likely to vary from finer grained ash fall to coarser grained pumice. It is important, therefore, to appraise the quarrying process in conjunction with the specific deposit type.

The cu.vol.% of <15 µm for individual quarries grouped by mafic, intermediate and felsic magma types (Figures 4.5-4.7) show a variation between different sample types (drilled, blasted, raw, accumulated, finished) both within and between individual quarries. As there are only 2-7 samples analysed for each quarry there is not enough data to pick out trends from individual quarries. A comparison by sample type is shown in Figure 4.8 which shows that overall, drilled samples from mafic lava flows (A) appear to contain more finer-grained material than is contained in raw material from felsic quarries (B). Specifically, the drilled dust range is 3.3-16.3 cu.vol.% <4µm and 8.3-27.5 cu.vol.% <10µm, whilst the raw felsic dusts range is 1.7-6.7 cu.vol.% <4µm and 2.77-10.9 cu.vol.% <10µm.

The finished product across all magma types (C) and dust accumulated on processors from active quarries (D) also showed a broad variation in data, further substantiating that the deposit type and mode of emplacement of the material play a role in the resultant quantities of <15µm.

The averaged data of different samples types, categorised by the mode of emplacement (lava flows - 3 mafic quarries; air fall deposits - 3 felsic pumice quarries; and PDCs - 3 intermediate quarries) shows little distinction (Figure 4.9). There is a large error associated with the averages and therefore distinctions between likely <15 µm content cannot be made on the basis of sample "type" even when comparing samples from similar deposits.

The drilled material from mafic lava flows and quarry floor samples from PDCs contained the most ≤10 µm material overall thereby potentially posing a respiratory hazard that would differ from most mafic volcanic eruptions where the ash is often (but not always) coarse. The intermediate PDC samples are potentially more likely to contain crystalline silica than the mafic samples (discussed as part of hypothesis 4, below). The mafic samples are, however, more likely to be comprised of iron-bearing minerals such as pyroxenes and amphiboles (compared to intermediate samples); and these have been implicated in the generation of hydroxyl radicals where poorly uncoordinated surface iron ions are present (Horwell *et al.*, 2007). The samples which contained the highest quantities of respirable material informed the selected for analysis in Chapter 5 where the capacity for particle surfaces to release iron and associated production of free radicals, as well as the potential toxicity of crystalline silica is explored.

It is therefore not possible to constrain any potential differences between the proportions of thoracic or respirable material within different quarry samples in this suite due to the great variations between different sample types and also between quarries for the same sample types.

2) *The proportion of thoracic (<10µm) and respirable (<4µm) material within volcanic quarry dust differs from that within erupted ash of the same magmatic composition.*

Mafic eruptions tend not to be highly explosive and, even when they are, they generally produce ash with <5 cu.vol.% respirable material. Exceptions to this have recently been

observed in the grain size of ash erupted from Grímsvötn (2010) volcano (Horwell *et al.*, 2013a) as well as Pacaya (1992) and Cerro Negro (1995) (Horwell, 2007). As shown in Figure 4.10, the range of grain size distributions for the <15µm fraction of mafic quarry dusts are broadly comparable with that of the range of mafic volcanic ash; there were three quarry samples which contained up to 5.2 cu. vol. % more <4µm with drilled samples the finest on average (Figure 4.9). There was also a variation in grain size within the andesitic quarries, with accumulated dust on processors generally being finer than finished product (Figure 4.9) but, again, the samples all fell in the range expected for volcanic ash of that composition. The grain size distributions of the felsic quarry samples were mostly coarser than felsic explosive ash samples but this is not surprising as the quarry samples were mostly derived from air fall ash or pumice and were not drilled or blasted to produce fine-grained samples, although some crushing occurred at the pumice and obsidian quarries.

These data highlight the fact that workers in volcanically active areas can be dually exposed to volcanic particulate of a comparable quantity of cu.vol.% of lung pertinent material, both from quarrying and from ash-fall. This scenario exists on Montserrat (although ash-fall on the island has not occurred since 2011) which is particularly concerning as the Soufrière Hills ash is often fine-grained and may contain up to 23 wt. % crystalline silica (Horwell *et al.*, 2014, Horwell *et al.*, 2013b). Occupational limits on dust exposure are set on the basis of an 8-hour time-weighted average (based upon a typical working shift) and are higher (allowing for greater exposure) than limits for environmental exposure which is based upon a 24-hour time weighted average. Such limits may not be appropriate for those who are exposed to volcanic particulate through their quarry work and who are further exposed to volcanic ash fall at home and/or work (see Chapter 6 for a full discussion on dual exposure). Both the Auckland Volcanic Field and the Taupo Volcanic Zone are historically active (Mt. Tongariro experienced minor eruptions in 2012) and so there is potential for dual exposure in these areas also, and no doubt in other locations globally, where volcanic deposits are mined both during and following eruptions, e.g. Merapi, and Kelud Indonesia 2010 and 2014, where fresh lahar and PDC deposits are being quarried (Damby *et al.*, 2013, de Belizal *et al.*, 2013) and material from the 1471-79 eruption of Sakurajima (Hillman *et al.*, 2012).

3) Volcanic quarry dust has a differing morphology to that of erupted ash.

Studies into fracture propagation in rocks indicate a close relationship with the internal structure of the rock and its rock grains and minerals (Guimaraes *et al.*, 2007). Fine-grained rocks develop acicular fractures which do not intersect, whilst rocks with coarsely cemented grains develop networks of macroscopic fractures (Guimaraes *et al.*, 2007). Therefore, some rock types produce a higher percentage of platy or elongate particles during mechanical fragmentation (Raisanen & Torppa, 2005). Here the morphology of quarried particles was analysed in consideration of these mechanical fragmentation factors, as some morphologies are potentially of greater health concern than others (Chapter 2, Section 2.6.2). Different magmatic conditions and differing extraction techniques could potentially give rise to varying morphologies and results here are compared with existing data for volcanic ash.

There was little variation in morphology among quarried volcanic samples at the respirable scale, regardless of magma type or extraction technique. Particles are blocky and angular, with fine particles often adhered to larger ones. Analysis of aspect ratio also revealed little variation between samples on average (with a greater tendency towards equant rather than elongate particles (Table 4.13); however, there was some variation within samples themselves. There were very few fibre-like particles and some glassy particles still retained bubble surfaces, and this was particularly noticeable for the pumice samples. These morphological characteristics are identical to those observed for volcanic ash (Damby *et al.*, 2013, Hillman *et al.*, 2012, Horwell *et al.*, 2013a, Horwell *et al.*, 2010a). The aggregation of particles was frequently observed, with many smaller particles adhering to larger ones. This is common in erupted volcanic ash with the particles adhering due to electrostatic attraction, moist adhesion, and formation of hydrometeoric water (Brown *et al.*, 2012); for quarry dusts, as they are not erupted particulate, it is likely that the aggregates are held together electrostatically. This has implications for lung health as electrostatic charge is one method of deposition in the lung (Chapter 2, Section 2.5.1 and Figure 2.2) and is discussed further in Section 4.6.2.

Despite differences in the fragmentation process between quarry dust and volcanic ash, there was little variation in morphology at the respirable scale. There was

also little difference between individual samples types across differing deposits and extraction techniques.

4) *Volcanic quarry dust contains abundances of crystalline silica which are similar to volcanic ash of a comparable eruption type.*

The crystalline silica content varied within and amongst quarries, depending on the original magmatic composition of the material and, in the cases of quarries of intermediate and felsic magmas, of the specific volcanic setting from which the deposit was derived.

The mafic quarry samples contain virtually no crystalline silica and only Flat Top contained ~1 wt.% quartz, which is not unexpected as the deposit is a tholeiitic basalt, subject to silica oversaturation.

Each of the intermediate (andesitic) quarries are excavating deposits which contain substantial quantities of crystalline silica, however, the variation of the specific polymorphs within individual quarries was low, which suggests that the extraction and processing did not cause the crystalline silica to fractionate and that differences amongst quarries are likely due to the deposits' origin and history. Overall, the quarries extracting Soufrière Hills PDC deposits and lahars contained 9-12 wt.% cristobalite and 2-5 wt.% quartz in comparison to the Little Bay deposits (quarried from the Silver Hills complex) which contained ~3 wt.% cristobalite and 15-16 wt.% quartz. This compares with 12-15 wt.% cristobalite in the Soufrière Hills dome collapse ash samples used in this study (Table 4.12) and up to 23 wt.% cristobalite throughout the entire eruption, which has displayed a much broader range (Horwell *et al.*, 2014).

It is likely that the ratio of quartz to cristobalite in the Montserrat samples is a factor of the age of the deposit, with the deposits derived from the current Soufrière Hills eruption (Trants and Belham Valley), containing more cristobalite, and the older deposits at Little Bay containing more quartz than cristobalite. This ratio is illustrated by location in Figure 4.30 (overleaf).

Cristobalite is meta-stable at ambient temperatures and pressures but persists in the environment due to the considerable activation energy required for the reconstructive transformation of cristobalite to low-quartz (Deer *et al.*, 1992). Ostwald's rule of stages shows that the first phase to crystallize is the thermodynamically unstable polymorph, which will subsequently re-crystallize to form thermodynamically stable phases (Nyvlt, 1995). Recent work by Horwell et al. (2013b) on the nature of crystalline silica from the Soufrière Hills volcano, showed that dome rock, dating from 174 k.a. B.P., still contained un-altered prismatic cristobalite. This indicates that, even over timescales of hundreds of thousands of years, vapour-phase cristobalite may not transform to quartz. However, the same sample also contained quartz as a devitrification product in areas where the groundmass glass had totally devitrified. The authors conclude that, in some environments, cristobalite formed by devitrification of glass can undergo reconstructive transformations to quartz (requiring breaking and reforming of bonds in the crystalline structure). In a volcanic dome, this re-crystallization could for example, be initiated by heating and throughput of volatiles related to, for example, the new injection of magma into the dome (Horwell *et al.*, 2013b). It is not clear where the activation energy for such a transformation occurred in the Little Bay samples. It is possible that hydrothermal fluid alteration occurred, but the age of the Silver Hills (from which the quarry is excavating) is much older (1.16 ±46 k.a. B.P. (Harford *et al.*, 2002)) than the samples which were studied by Horwell et al., therefore, over these timescales, transition to quartz from vapour phase or devitrification cristobalite (which may be less structurally complete than vapour-phase cristobalite) may be possible without injection of a heat source.

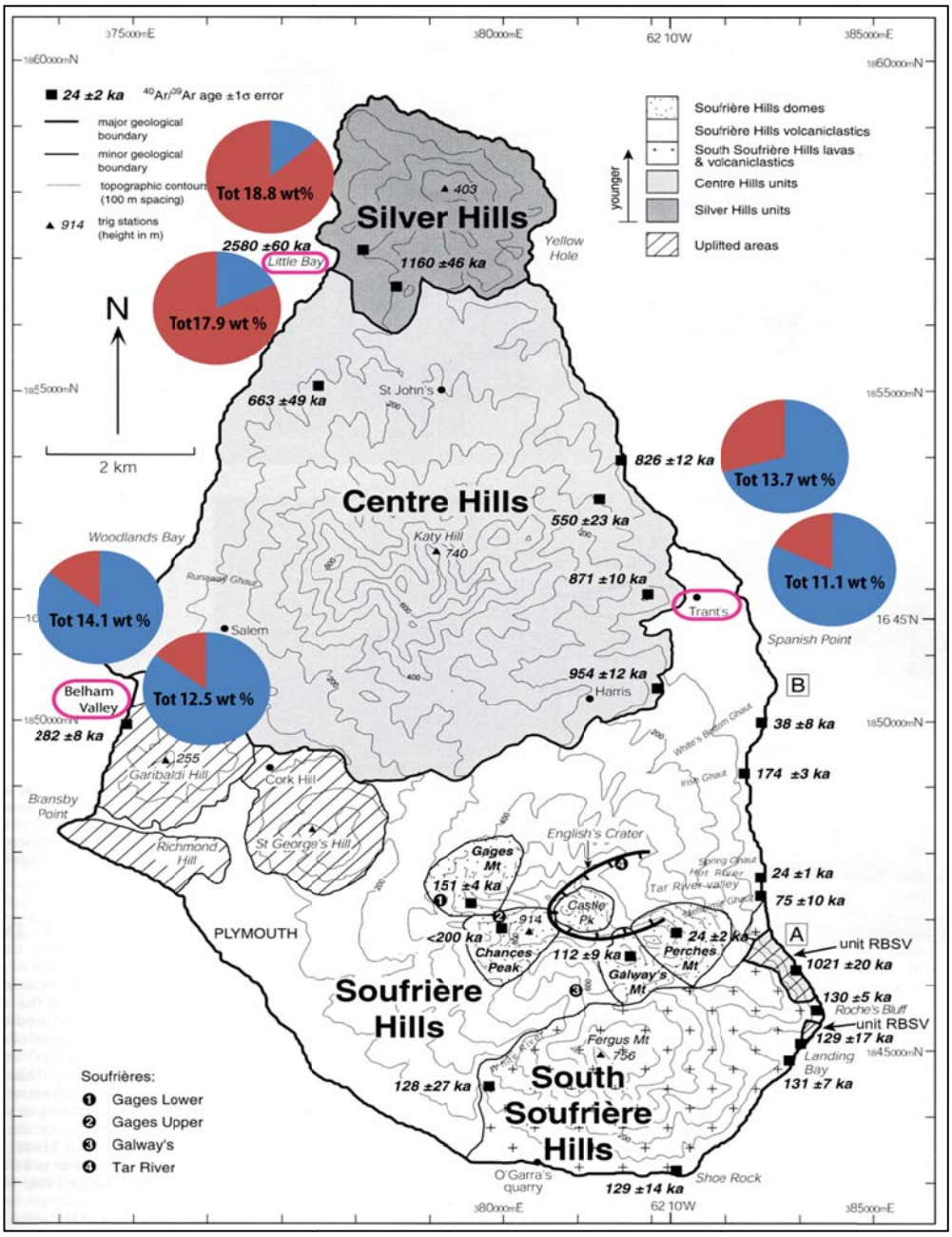


Figure 4.30 The proportions of cristobalite (blue) and quartz (red) in different samples at Little Bay, Trants and Belham Valley quarries in Montserrat. Map modified from Harford et al., (2002).

At this point, it is not clear whether the ratio of quartz to cristobalite in these samples is critical for respiratory hazard assessment. Studies of crystalline silica toxicity have yielded mixed results in respect to the different polymorphs (IARC, 1997) but the weight of evidence, from previously published toxicity studies, suggests that quartz and cristobalite are equally toxic (Driscoll, 1995, Fubini, 1998a, Hemenway *et al.*, 1990, Meldrum & Howden, 2002). The toxicity and surface reactivity of these samples is tested in Chapter 5.

Clay derives from the weathering of feldspar and was only present in samples from Little Bay, which are 1-2 k.a. older than those from Trants or the Belham Valley. This has implications for potential toxicity as clays and other minerals were often observed to occlude quartz grains which would make their surface unavailable for reaction in the lungs. Clay, feldspar and volcanic glass are all rich in aluminium which, as discussed previously (in Chapter 2), may act to reduce the toxicity of crystalline silica in the lung. In particular, it is thought that clay occlusion of quartz in coal dust may prevent silicosis in coal miners (see Chapter 2, (Stone *et al.*, 2004, Weller & Ulmer, 1972)). The retention of such particles in the lung (and the speed at which such occluding clays are dissolved) is a controlling factor in the potential for such particles to cause damage to lung cells (Oberdorster *et al.*, 1994). In contrast, the samples from Trants and the Belham Valley do not contain clays but their surfaces are also occluded by glass, feldspar and other minerals. Horwell et al. (2012) studied polished sections of Soufrière Hills volcano ash in detail and found that very few cristobalite crystals were not occluded to some degree. The occlusion of crystalline silica in the Soufrière Hills samples could, therefore, substantially alter their toxicity (Horwell *et al.*, 2012). Horwell et al. (2012) also showed that inherent factors of the cristobalite may also play a role; the cristobalite was found to have up to 4 wt.% Al and Na, which might sufficiently alter the surface of the particles in the lung environment to affect their surface reactivity (Horwell *et al.*, 2012). This is being explored in another project, at present, where synthetic cristobalite is being manufactured with varying levels of impurities (Nattrass, In prep.). These samples will be systematically tested for variations in *in vitro* toxicity depending on their composition.

The felsic pumice and perlite samples mostly proved to contain less crystalline silica (≤1.5 wt.% cristobalite and ≤6 wt.% quartz) in comparison to the andesitic PDCs samples. Coupled with their comparatively coarser grain size, these samples should – theoretically at least – be considered less of a hazard. The obsidian dome rock samples from Henderson quarry, however, contained very high levels of crystalline silica in the form of cristobalite and tridymite. The total crystalline silica content for these samples varied from 18 to 29 wt.%, suggesting that crystalline silica content was not uniform throughout the deposit or varied between material extracted and processed. The majority of the cristobalite was in the form of spherulites (Close, 2012), which are circular clusters of crystals formed of fibrous intergrowths of cristobalite and potassium feldspar

which may be fragmented during extraction and processing. However, the intergrown nature of the cristobalite and feldspar indicates that un-occluded cristobalite particles are unlikely but the larger tridymite crystals may well display fresh surfaces following fragmentation, which has implications for the potential toxicity of the particle surfaces. As described by Horwell et al. (2012), fragmentation of dome rock containing crystalline silica intergrown with groundmass or devitrification minerals, will create particles which will not be composed of pure crystalline silica, due to continued adherence of the neighbouring minerals to the crystal surfaces.

It is difficult to compare the felsic quarry samples with analogue ash samples because there have been so few rhyolitc eruptions in recent times. Chaitén volcano, Chile, erupted in 2008; the initial explosion disrupted an existing, ancient obsidian lava dome with the resulting ash containing up to 7 wt. % cristobalite (although most samples contained around 2 wt. %)(Horwell *et al.*, 2010a). Horwell et al. (2010a) believe the cristobalite derives from disruption of the dome, whereas, Reich et al. (2009) hypothesise that the cristobalite nanofibres they observed may have formed through high-temperature vapour-phase reactions within the explosion column. Following an initial explosive phase, rapid obsidian dome growth occurred and analysis of ash generated during collapses of the dome found a distinct increase in cristobalite content (up to 14-19 wt % Horwell et al. 2010a, Table 4.4 in this chapter). In 2011, another rhyolitic volcano, Puyehue Cordon-Caulle (PCC; also in Chile) erupted. In the absence of a dome, the ash was found to be almost entirely lacking in crystalline silica (<2 wt.%, Horwell, unpublished data). Comparing the quarried pumice samples to the PCC eruption shows similar quantities of crystalline silica; as does comparison of the quarried obsidian dome samples with the Chaitén dome building phase. Henderson quarry samples contained tridymite, which was not observed at Chaitén but both sample sets contained unusually high quantities of crystalline silica, indicating that this eruption style is potentially one of the more hazardous, both in terms of ash inhalation and exposure to extracted quarry dust.

4.6.2 Comparison with non-volcanic quarried samples

Six samples of non-volcanic material (four greywacke samples from Hunua and two sandstone samples from Moneystone) were included alongside the broad suites of quarried volcanic dusts and volcanic ash. Whilst not part of the main investigation, they have been studied as a non-volcanic comparison to help indicate whether volcanic quarry dust poses a unique hazard.

The greywacke samples (HU_01 to HU_04) contained comparable amounts of respirable dust (6-9 cu.vol.% of <10 µm material) to the volcanic quarries, however the sandstone quarry dust contained significantly higher amounts of respirable material; the raw sample (MSR) contained as much as 55.6 cu.vol.% <10 µm material which is of potential concern because XRD analyses revealed it to be almost pure quartz (~98 wt.%). It is worth noting that the particles in this sample had an unusual, platy morphology which might alter the deposition of particles in the lung. The processed sample (MSCr) contained substantially less respirable dust (18.0 cu.vol.% at <10 µm), indicating fusing and aggregation of the platy particulate during the heating process; however, it did result in these particles having a higher surface area. As this sample is composed of near-pure cristobalite (99 wt.%) this is also a sample of potential concern. In comparison to the volcanic quarry samples (and to Hunua), these samples are both much finer and richer in crystalline silica, so it is clear why agencies such as IARC have chosen to focus their research and controls on such rock types. Furthermore, it is also clear that volcanic quarry samples do not have physicochemical characteristics to match this level of concern.

The volcanic quarry dusts, however, should not be dismissed as not being worthy of further investigation for potential health hazard because, whilst they were coarser and less rich in crystalline silica, they were still capable of penetrating the lungs and some samples (notably those from dome-forming volcanoes) contained up to 28 wt.% crystalline silica. Whilst mineralogical and physical characterisation is a key starting point, the metrics outlined here cannot indicate the likely response of the human lungs to these dust samples. It is therefore imperative to test them further using toxicological and surface-reactivity analyses; such tests are conducted in the next chapter.

4.6.3 Comparisons of physicochemical parameters and further outcomes

No single parameter influences potential hazard, but rather a combination of inter-related factors combine to affect particle toxicity. Several health-pertinent parameters have been investigated here individually; however, it is also useful to try to determine the extent of inter-relation although with mixed natural dusts this can be challenging, due to sample variation as demonstrated.

Grain size and surface area

Grain size can be linked with surface area, as generally, surface area should increase as particle size decreases, although this relationship can be substantially affected by parameters such as porosity and the quantity of fine-grained particles. A correlation between grain size and surface area can be useful because determining surface area, especially on limited sample quantities of the <10 µm fraction, is more challenging than determining grain size. Surface area is an important driver of surface reactivity and previous work on both <1mm 'bulk' and the respirable fraction of ash from Montserrat has shown differences in surface area. Horwell et al. (2003a) used N_2 adsorption to determine the surface area of three bulk samples of ash from the Soufrière Hills volcano, which had lower surface areas (1.5, 1.5 and 1.8 m^2/g) than their respirable counterparts (3.6, 3.7 and 7.5 m^2/g respectively).

To determine if there is a relationship between grain size and surface area for volcanic quarry samples, Fig. 4.31 shows the amount of ≤10 µm material versus the surface area. There is no positive correlation of increasing surface area with increasing abundance of ≤10 µm particles indicating that surface area is not controlled by grain size for volcanic quarry samples and they cannot, therefore, be used as a proxy for one another when only one analysis type is possible (for example surface area is more difficult to measure than grain size distribution). It is likely that, in the case of these samples, factors other than grain size are influencing the surface area, for example the quantity of fine-grained particles, the porosity of the samples or the presence of secondary, alteration products, such as clays which are known to have high surface areas. For example, the samples with very high surface area from the Flat Top mafic lava quarry (8.3

and 10.8 m^2/g) contain comparatively little ≤10 µm (8 and 3 cu.vol. %, respectively); however, the clays chlorite, smectite and illite have been found in this deposit (Nicholson *et al.*, 2000) and the presence of clay was determined here by SEM (Section 4.4.4). Ticknor and Saluja (1990) analysed the surface area of different powders of a comparable grain size including basalt (106-180 µm), quartz (106-180 µm), illite (75-180 µm) and chlorite (106-180 µm); they found that the clay minerals had a BET N_2 adsorption surface area of 2.38 m^2/g for chlorite and 16.3 m^2/g for illite, whilst basalt and quartz were much smaller at 0.58 m^2/g and 0.10 m^2/g respectively.

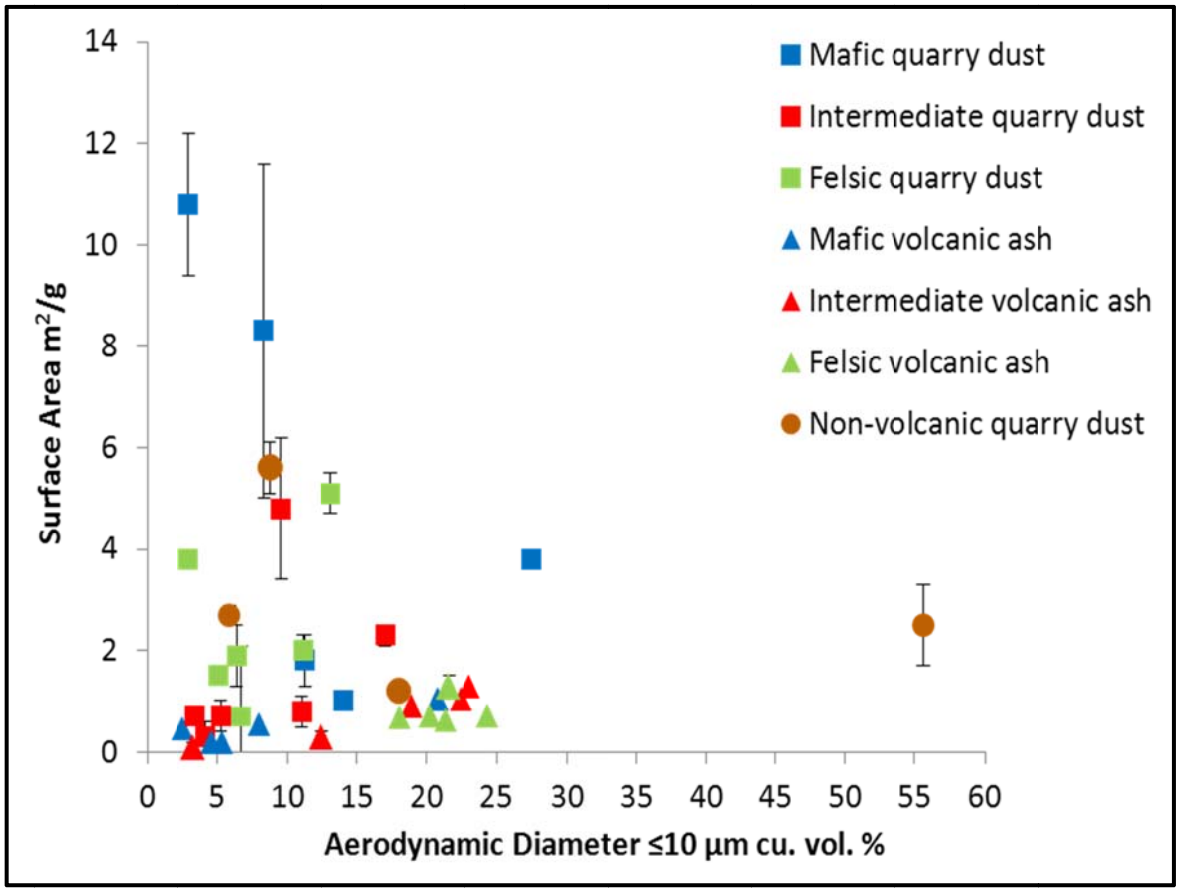


Fig. 4.31 The amount of ≤10 µm material (cu. vol. %) versus the surface area (m^2/g).

This lack of correlation also prevents an estimate of the likely surface area of the separated ≤10 µm fraction, which is likely to have a larger surface area than that listed in Table 4.8 for the bulk sample and may play a role in the haemolytic potential of the ≤10 µm separated fraction.

Bulk SiO_2 and Crystalline Silica Content

Some correlation may be observed between SiO_2 content and magmatic quartz, which would potentially allow for bulk composition to be used as a likely indicator of potential crystalline silica content, although correlation between SiO_2 and cristobalite is unlikely. Quartz may be magmatic or may form as a precipitate from hydrothermal fluids (Horwell *et al.*, 2013b); however, magmas which do not contain much SiO_2, are unlikely to contain large quantities of quartz. Conversely, cristobalite is not a primary magmatic phase, but typically forms as a hydrothermal product, by devitrification (by solid-state crystallisation from amorphous volcanic glass) or by precipitation from a vapour phase; the latter two formations have been observed at the Soufrière Hills volcano (Horwell *et al.*, 2013b). Figure 4.33 shows SiO_2 (determined by XRF) against A) cristobalite content and B) quartz content (determined by XRD). As noted, magmas which do not contain much SiO_2 are unlikely to contain large quantities of quartz or cristobalite; here the mafic magmas which contain the least SiO_2 also contain little quartz and no cristobalite, the quarry exception is the tholeiitic sample which contained about 1 wt.% quartz. The intermediate and felsic magmas contain more SiO_2 and concurrently both more quartz and more cristobalite but a positive correlation is not observed; this indicates that SiO_2 content cannot be used as an indicator of the likely crystalline silica content, especially in settings where these polymorphs are likely to form post-eruptively.

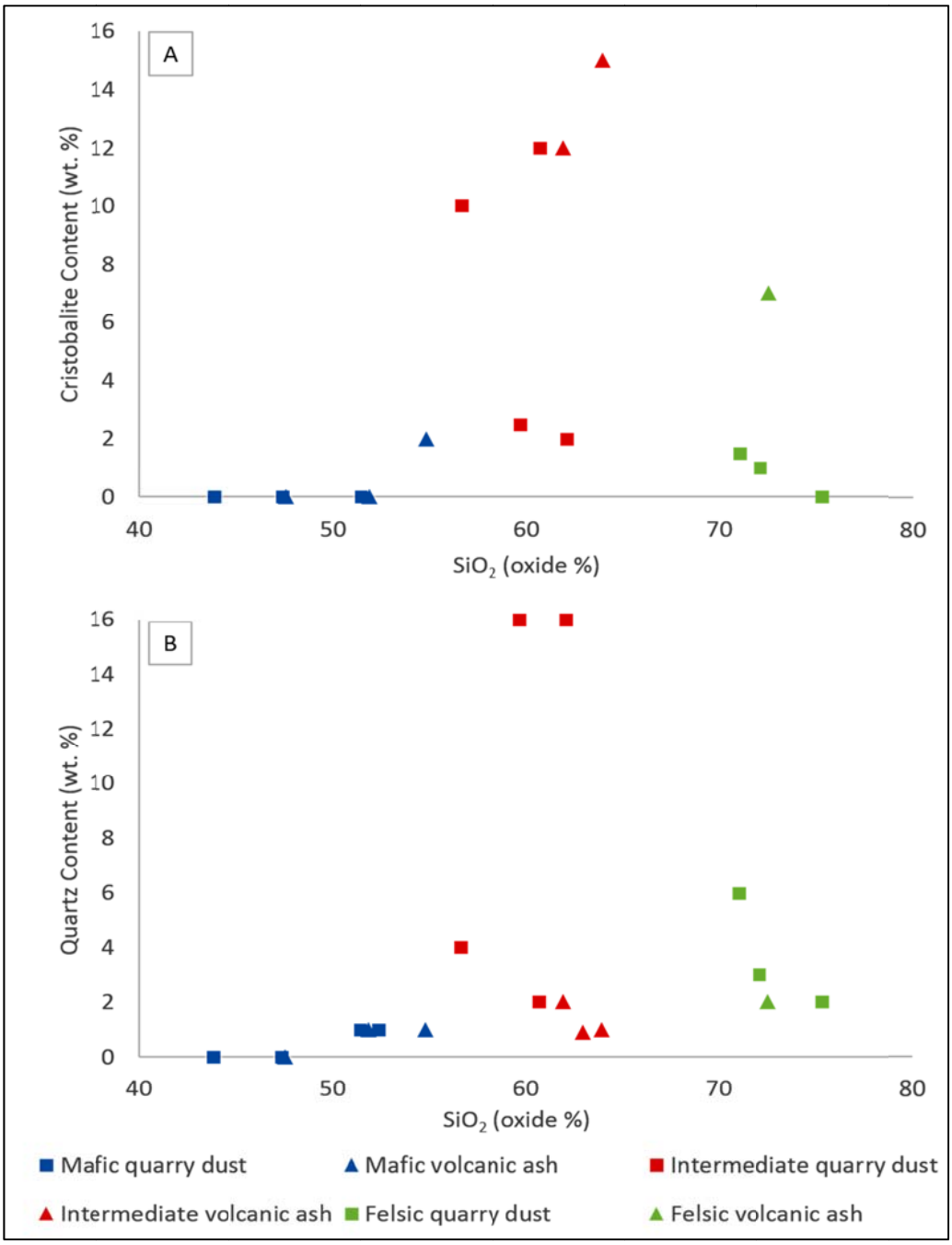


Figure 4.33 A) Cristobalite content and B) Quartz content (wt. %) versus SiO_2 (oxide %).

Crystalline Silica Content and <10µm Content

The crystalline silica content is plotted against the <10 µm fraction in Figure 4.34 for a variety of intermediate (red) and felsic (green) magmas. Overall, there is no correlation, however, for individual sub-sample sets some poor positive correlation may be observed, for example the intermediate dome collapse ash and the intermediate PDC quarry dust.

Horwell (2003b) found the preferential fractionation of crystalline silica in the finer fraction of dome collapse ash, which is an effect that might be seen here, however, with only two samples it is not possible to infer a correlation.

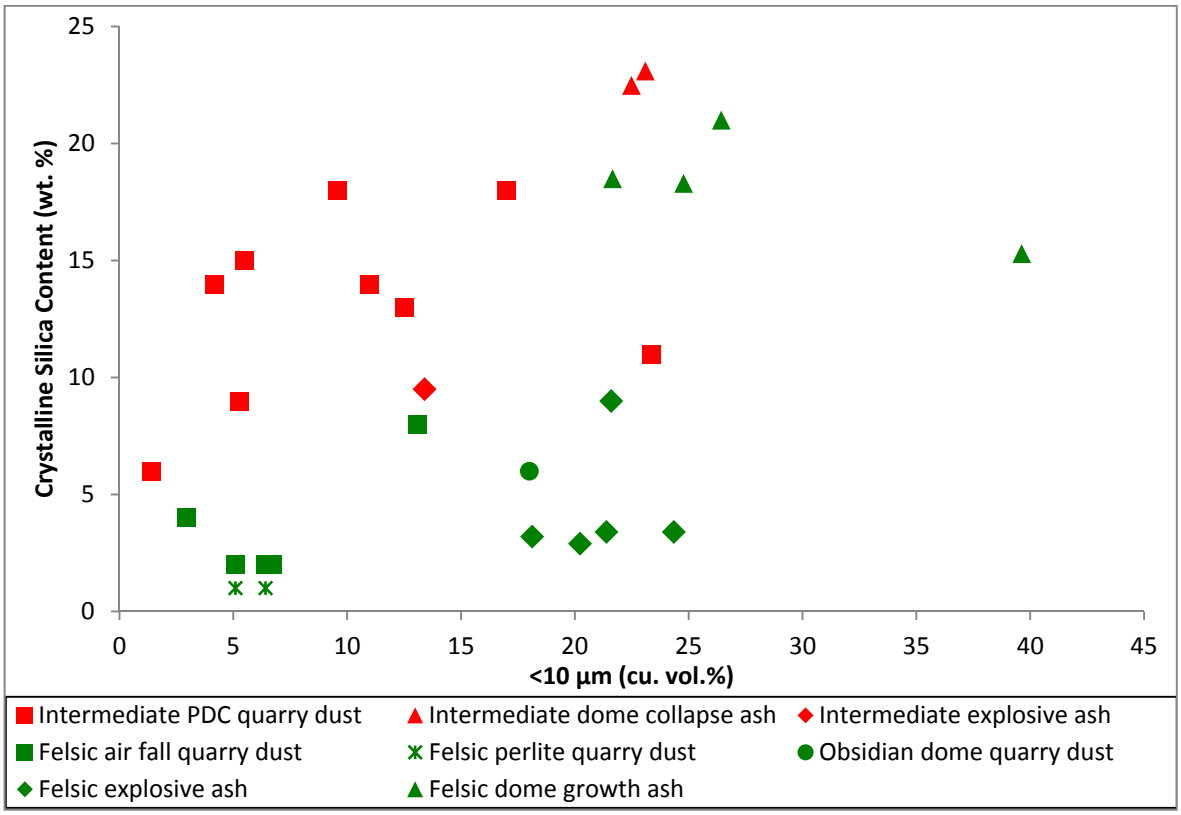


Figure 4.34 A) Cristobalite content and B) Quartz content (wt. %) versus amount of ≤10 µm material (cu. vol. %)

Aggregation of fine particles:

As noted in hypothesis 3, Section 4.6.1, SEM analysis revealed aggregates of fine particles adhering to larger particles, which are likely to be held together by electrostatic attraction. This has implication for inhalation as electrostatic charge is one potential pathway for particle deposition in the lung and experiments with human subjects show that the lung deposition of inhaled aerosol can be substantially increased by the electric charges carried by the individual particles (Vincent, 1985). This is particularly significant for fine particles which can penetrate deeper into the lung, and which have a larger charge-to-mass-ratio because of their larger surface-to-volume ratio which therefore makes them more likely to aggregate as a result of electrostatic forces (Gilbert et al.,

1991). Electrostatically aggregated particles are unlikely to 'earth' in the lung; the decision was taken, therefore, that samples tested for haemolytic potential in chapter 5 should not be disaggregated prior to analysis, so that they remained as close as possible to the state they occupy in the lungs.

4.7 Conclusions

The mineralogical analyses conducted here suggest that there are two key types of quarried volcanic material which pose the greatest potential threat:

i) Drilled mafic material

ii) Finer-grained intermediate-felsic material from dome-forming volcanoes

This highlights two critical considerations which must be made when assessing hazard: i) the nature of the quarrying work being undertaken and ii) the type of deposit and its mode of emplacement. The drilled mafic material is a potential hazard because it produces a substantial quantity of respirable material which may potentially have reactive iron on particle surfaces (the latter to be investigated in Chapter 5); this is a function of the deposit type and mode of emplacement (solid mafic lava flow) as well as the mode of extraction (drilling). The finer-grained intermediate-felsic material from dome-forming volcanoes is a potential hazard because it can also contain a substantial quantity of respirable material which may be rich in crystalline silica, a known mineral of health concern. This also a function of both deposit type (finer grained samples included those from ash-fall and PDCs) and mode of emplacement (dome-forming eruptions in this study are richer in crystalline silica than their amorphous counterparts) as well as the method of extraction (whilst excavation and screening are not as energy-intensive as drilling, the starting material is much more friable).

This chapter also highlights that there is variation within quarries between the quantities of respirable material in different sample types (i.e. raw, processed, finished) both within and between quarries. It is important therefore, to determine whether different role in the quarry are associated with different exposures and to determine the appropriateness

of limits for those dually exposed to quarry dust and ash. The exposure measurements and mitigation strategies employed are presented in Chapter 6.

Whilst size, shape, surface area, crystalline silica content and silica occlusion are important factors to characterise when assessing the potential hazard of quarried particulate, they need to be considered along with exposure data and investigations of the surface reactivity and toxicity of the particles, in order to address both sides of the 'structure-toxicity' relationship. There are many factors which contribute to the potential pathogenicity of particles (as outlined in Chapter 2) and, as such, it is difficult to predict how they might behave in the lungs without testing for their surface reactivity and potential toxicity. These factors are explored in the next chapter.

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Chapter 5 – The Surface Reactivity and Potential Toxicity of Volcanic Quarry Dust

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5.1 Introduction

This chapter investigates the surface properties and reactivity of volcanic quarry dust and its resultant toxicity. In the previous chapter, various physicochemical parameters were investigated to determine whether the dust particles were able to penetrate the lung and whether they possessed any physical or compositional characteristics with the potential to cause toxicity. In this chapter, the surface properties of the dusts are investigated and appraised for their reactivity and potential to cause oxidative stress and cellular injury in the lungs. This was assessed through measurement of surface reactivity (in the form of hydroxyl radical generation), lipid peroxidation and haemolysis.

5.1.1 Surface properties and reactivity

The effects of insoluble particles in the lung (such as mineral dusts produced in quarries) depend upon surface properties of the solid because it is this surface which will be the site of any interaction with lung components. If a particle has a reactive surface then a particle with a larger surface area will cause a greater reactive response than a similar particle with a smaller surface area (Duffin *et al.*, 2007, Fubini & Otero-Areán, 1999).

The fracturing of particle surfaces through rock fragmentation, for example by drilling, blasting or crushing, may generate radicals; these are atoms with unpaired electrons. Radicals are highly reactive, in a bid to complete the electron pairing, taking electrons from nearby molecules which, in the lung, are likely to be cellular components (Flaschka, 1969). Surface radicals may occur on freshly-created dust particles; with silica for example, the silicon-oxygen bond can be homolytically cleaved, resulting in dangling bonds. Heterolytic cleavage may also create a reactive surface, in the form of a cation and an anion, as illustrated in Figure 5.1 (Fubini *et al.*, 1995a). This produces a very reactive surface which tends to either recombine (with the formation of strained reactive bridges) or react with atmospheric components (creating active oxygen species) (Fubini *et al.*, 1995a). Free radicals may also be generated within the lungs once the particle is inhaled and brought in contact with lung fluids (Cohn *et al.*, 2006). One of the most important radicals, in terms of cell damage, is the oxygen-centred hydroxyl radical (HO•), formed by the catalytic action of transition metal ions, such as iron, through the Haber Weiss Cycle (shown in Reaction 5.1 below). The iron can be present in trace impurities on the surface

of minerals such as crystalline silica in intermediate to felsic magmas, or on surfaces of dust particles quarried from iron-rich mafic magmas (Cohn *et al.*, 2006).

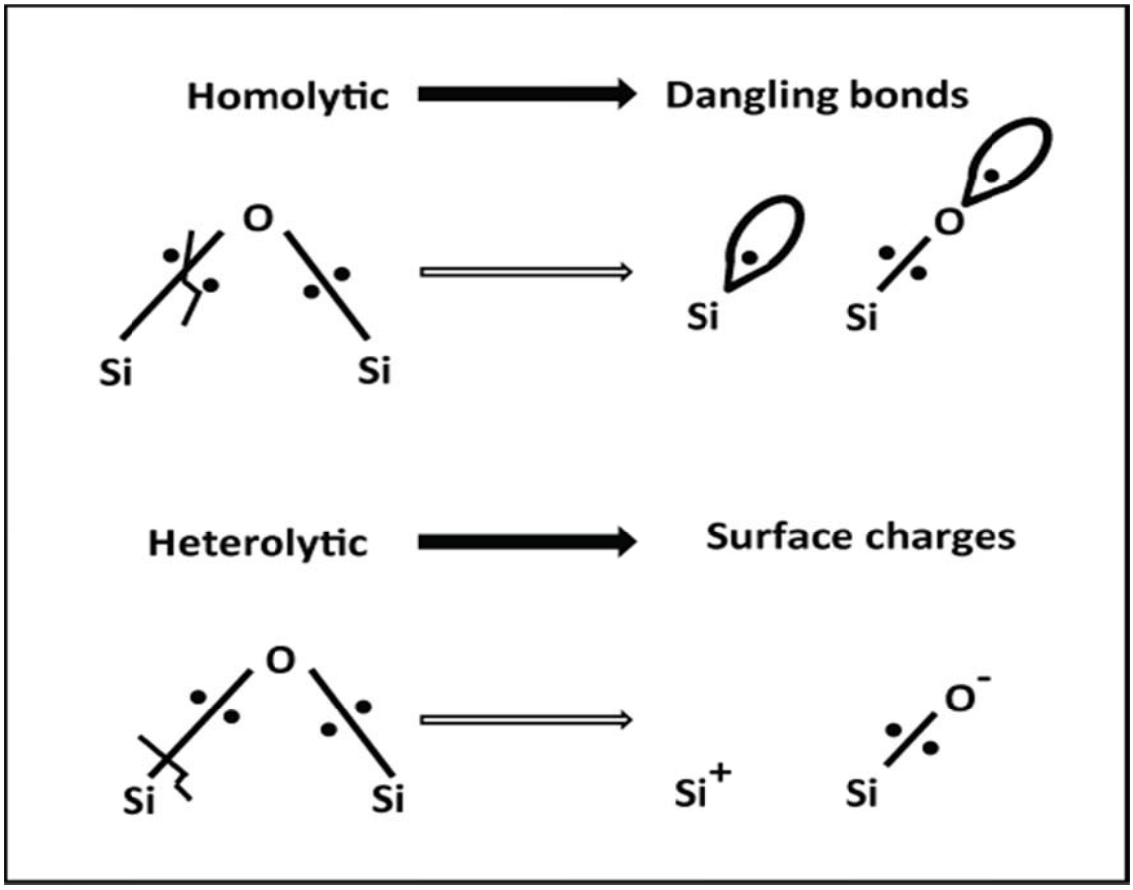


Figure 5.1 Cleavage of the silicon-oxygen bond after mechanical grinding. After Fubini et al., (1995a).

1) Fe^{3+} + reductant → Fe^{2+} + oxidised reductant	In the presence of a reductant (e.g. ascorbate) trivalent iron is converted to divalent iron.
2) $Fe^{2+} + O_2 \rightarrow Fe^{3+} + O_2^{-\bullet}$	Divalent iron and oxygen react to form the superoxide radical.
3) $O_2^{-\bullet} + 2H^+ + e^- \rightarrow H_2O_2$	The superoxide radical reacts with hydrogen cations to produce hydrogen peroxide.
4) $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO\bullet$	Divalent iron undergoes the Fenton reaction in the presence of hydrogen peroxide producing the hydroxyl free radical. However the Fenton reaction may also occur by reaction of Fe^{2+} with endogenous H_2O_2, thereby bypassing steps 1-3.

Reaction 5.1 The Haber Weiss Cycle (Fubini & Otero-Areán, 1999)

Hydroxyl radicals have a propensity to capture a replacement for their missing electron by extracting a hydrogen atom from C-H bonds within endogenous molecules such as DNA and lipids, causing damage and lipid peroxidation (Fubini *et al.*, 1995a). Iron-catalysed free radical generation has been determined to play a role in both lung inflammation and carcinogensis (Kane *et al.*, 1996). The Fenton reaction (Reaction 5.1, step 4) can be replicated in the laboratory to test the propensity of a dust to generate hydroxyl radicals in the lung.

5.1.2 Particle surfaces, oxidative stress and cell membranes

Oxidative stress describes the imbalance resulting from an excess of pro-oxidants compared with antioxidants (Kelly & Mudway, 2007). Exposure to particulate matter can cause disruption in the cellular redox states in the lung by initiating redox-sensitive signalling pathways which lead to inflammation. This response is triggered by redox active metals (such as Fe) adsorbed on the surface of the inhaled particles; the resulting oxidation reaction leads to the production of cytotoxic reactive oxygen and nitrogen species (ROS, RNS), such as the hydroxyl radical. The airway inflammation this leads to then causes generation of oxidants produced by recruited phagocytes propagating the cycle of oxidative injury (Kelly & Mudway, 2007).

There is an abundance of membrane phospholipids at sites where ROS form, which makes them attainable, endogenous sources for lipid peroxidation (Goulart *et al.*, 2005). Lipid peroxidation is a chain reaction instigated by free radicals and resulting in the catalytic production of several equivalent lipid peroxides. Lipid peroxidation is involved in a variety of pathological conditions, including cancer (Goulart *et al.*, 2005).

Studies into surface reactivity by Fubini (1997) revealed that the potential toxicity of solid particles cannot be estimated on the basis of chemical composition and molecular structure alone (Fubini, 1997). At the surface of a crystalline particle, poorly-coordinated atoms and ions are present in specific locations following fragmentation, creating confined areas of marked reactivity. This is particularly salient for particles with the same bulk composition, as it is their micro-morphology (notably influenced by their mechanical history) which determines the types and quantity of active surface sites which, in turn, controls reactivity directed towards cells and tissues (Fubini, 1997). Studies of volcanic

ash reactivity by Horwell et al. (2003a) found that, during fragmentation of lava during explosion or dome collapse, particles are broken up into smaller fragments with larger surface areas. Particles may also be abraded rather than fragmented, however, which wears down the surface, exposing fresh surfaces, and increasing reactivity, but without altering the size or surface area substantially (Horwell *et al.*, 2003a). This is directly relevant in the generation of quarry dusts which may also suffer fragmentation and abrasion as they are extracted and processed. Therefore, the mechanical history of quarry dusts may affect their surface area and surface functionalities which may have significant bearing upon their potential toxicity.

5.1.3 Weathered surfaces and reactivity

Particles which have undergone leaching, by weathering from precipitation, for example, may have a slightly increased surface area due to empty cavities in the solid particle (Fubini, 1997). However, iron-catalysed surface reactivity is primarily affected by the oxidation state of the iron. Horwell et al. (2003a)found that weathered volcanic ash was substantially less reactive (in terms of hydroxyl radical generation) than freshly-collected ash, contained more Fe^{3+} and that grinding ash led to enhanced reactivity and surface area. This is relevant for quarry dusts which may have come into contact with rain or percolating water during their processing and storage, as well as during their lifetime within the original deposit. Research into the physicochemical properties of crystalline silica dusts and their biological responses (undertaken by Fubini et al. 1995 (Fubini *et al.*, 1995a)) revealed that wet grinding decreased a dust's capacity to produce radicals compared with dry grinding, as water assists in the reconstruction of the particle surface (Fubini *et al.*, 1995a, Volante *et al.*, 1993). It is suggested that the differences in the pathogenic response elicited by dusts are related to the mechanical weathering the dust particles have experienced and that this also controls the release of ROS, instigating oxidative bursts and lipid peroxidation (Fubini *et al.*, 1995a).

It is these three factors (fresh surfaces with dangling bonds, poorly coordinated atoms at the surface and chemical weathering of the surface) which are likely to be responsible for variability in the generation of hydroxyl radicals in particles with the same composition (Fubini, 1997). This highlights the importance of investigating the

pathogenicity of several sample types, even if their bulk chemistry, particle size and crystalline silica content are similar.

The potential toxicity of particles can be assessed through the haemolysis assay which determines the propensity of a particle to lyse the cell membrane of a red blood cell. Crystalline silica is a driver of haemolysis and this first-order toxicity test has been used to determine potential toxicity of volcanic ash (Damby *et al.*, 2013, Jones & BeruBe, 2011, Stone *et al.*, 2004, Wilson *et al.*, 2000).

In mixed dusts (such as those from coal mining), the crystalline silica content is not usually associated with pathogenicity unless there is >10 wt. % quartz in the sample (Buchanan *et al.*, 2003); and some studies have revealed low levels of pneumoconiosis amongst coal miners who were exposed to high levels of quartz (Borm & Tran, 2002). One mechanism to explain this is the presence of clays in low-rank coal dusts which inhibit the activity of quartz particles by either occluding the quartz particle surface or being present in close proximity to it (Dalal *et al.*, 1995, Stone *et al.*, 2004). Similarly, investigation of respiratory disease in the heavy clay industry revealed low disease prevalence despite high quartz concentrations (Love *et al.*, 1999). Clay minerals, especially ones which release aluminium ions, found on the surface of well-weathered quartz-containing particles are thought to reduce quartz toxicity (Love *et al.*, 1999). Certain clays (e.g. illite) are more effective at ameliorating this toxicity than others(Love *et al.*, 1999). Other clays, however, such as kaolin, are known to elicit a toxic response in the lungs (Love *et al.*, 1999, Wallace *et al.*, 1988). This has implications for volcanic quarry dusts which are not purely crystalline silica and some of which are ancient and will have been subjected to prolonged weathering, which may have clays introduced through breakdown of minerals such as feldspar. Although clays can ameliorate quartz toxicity they may also influence the haemolysis assay. Clays are known to be highly haemolytic with smectites generating more cell rupturing than silica (Oscarson *et al.*, 1986). These combined factors affecting surface toxicity have led to the postulation of several hypotheses, which this chapter aims to address.

5.2 Aims and Hypotheses

The overall aim of this chapter is to investigate the pathogenic response elicited by different volcanic quarry dusts and to compare this with both volcanic ash and non-volcanic quarry dusts. Specifically, the hypotheses to be tested and their justifications are:

1) *Dust from quarried mafic material exhibits greater surface reactivity, than dust from intermediate or felsic quarries.*

It has broadly been shown that mafic volcanic ash generates more radicals than intermediate or felsic volcanic ash, due to its increased iron content (Horwell *et al.*, 2007, Horwell *et al.*, 2003a).

2) *Drilling/blasting mafic lava produces dust which is more reactive than fragmentation of magma during mafic volcanic eruptions.*

The mafic quarries visited in this study are all mining deposits of solid lava which required drilling and blasting in order to extract material for aggregate production. The production of particulate in these quarries, therefore, was via a mechanism which had the potential to generate dust with different physicochemical characteristics from mafic ash generated during volcanic eruptions. In general, mafic eruptions generate coarse ash (with low surface areas) due to the low explosivity of the eruptions. Drilling and blasting of lava in quarries may produce dust which is finer-grained than magmatically-equivalent volcanic ash samples (Chapter 4 Section 4.4.2) and some had substantially higher surface areas than equivalent ash (Chapter 4, Section 4.4.3). Furthermore it is possible that fragmentation (as a result of drilling and blasting) will create different surface functionalities compared to fragmentation from magmatic explosion resulting in a difference in surface reactivity between quarried and erupted particulate. Also, samples exposed to the environment may have secondary phases such as clays weathered from feldspar which may also contribute to the haemolysis signal.

3) *Intermediate and felsic quarry dusts will generate more haemolysis than mafic quarry dusts.*

Crystalline silica is known to induce haemolysis (Clouter *et al.*, 2001) and in Chapter 4 it was found that some dust samples from intermediate and felsic magmas contained appreciable quantities of crystalline silica compared to mafic magmas which has a negligible content. It is likely therefore, that any haemolysis observed here will be instigated by samples which are richer in crystalline silica. The haemolytic potential of volcanic ash, conducted in recent studies (Damby *et al.*, 2013, Horwell *et al.*, 2013, Jones & BeruBe, 2011, Wilson *et al.*, 2000) has found to be lower, particularly in comparison to the DQ12 quartz standard commonly employed. As the mechanism for silica toxicity is unclear, it is difficult to predict whether the quarried volcanic particulate contains similarly low-toxicity silica.

4) *The extraction and processing of material produces dust with fresh surfaces which is more reactive than the dust accumulated on the quarry floor or the stockpile.*

A previous study (Horwell *et al.*, 2003a) showed that weathered volcanic ash surfaces are less reactive (in terms of hydroxyl radical generation) compared to those that are fresh. In quarries, dust accumulated on the floor or in the stockpile will have been exposed to substantial rainfall, likely to result in leaching of surface species and oxidation of iron. In addition, some processing involves the washing of particles during screening, so stockpiled deposits will have had further contact with water.

5) *Quarrying friable, intermediate deposits from pyroclastic density currents or lahars produces dust which is less reactive than erupted ash from the same source volcano.*

Samples of intermediate volcanic ash used in this study, from the Soufrière Hills volcano, were collected fresh upon deposition. Quarried Soufrière Hills samples, collected from pyroclastic density currents (PDC) and lahar deposits at Trants and Belham Valley respectively, had likely been exposed to percolating vapours and meteoric water (in the case of PDC deposits) and to channelled water flow (in the case of lahars), thereby potentially weathering the deposits, which would detrimentally affect the surface reactivity. In addition, Horwell et al. (2001, 2003b) showed that PDC and lahar deposits are coarser, and contain less crystalline silica than co-PDC ashfall deposits, due to

fractionation of the smaller, less-dense particles by elutriation into the lofting co-PDC plume (in the case of PDCs) or lahar flow, leaving a fines-depleted deposit.

It is probable that erupted ash (which is collected immediately) is more reactive because it will have retained the freshly fractured surfaces, is fines-enriched (Figure 4.10), and is not exposed to moisture except within the volcanic plume where it is likely to have a variety of elements adsorbed onto its surface.

5.3 Methodology

5.3.1 Sample Collection and Preparation

Samples were collected and prepared following the protocols outline in Chapter 4, Section 4.3.1, with cone and quartering used to obtain representative subsamples for each analysis.

5.3.2 Sample Selection

Volcanic Quarry Dust Samples

Due to the time-consuming nature of the surface reactivity analyses (HO• generation and Fe-release), specific (<1mm size fraction) samples were chosen for analysis from the wider sample set, based on their high content of respirable material and their representation of a variety of magma types (as determined in Chapter 4) with 5-6 samples from each magmatic group (mafic, intermediate, felsic) being selected. Each magma type included samples of both finished product and either raw material or, where this was not possible (as in Montserrat due to the extended volcanic exclusion zone), samples of dust that accumulated on the processor in lieu of raw material. This allows for the comparison of reactivity pre- and post-processing and, for this reason, the sample of perlite expanded in the UK by British Gypsum (BGEP) was also included.

Due to the known increased reactivity of mafic samples in respect to Fe-release and radical generation (Horwell *et al.*, 2007, Horwell *et al.*, 2003a, Horwell *et al.*, 2010b), three of the finest (drilled) quarry samples were selected (one from each of the mafic quarries) for a further lipid peroxidation test.

A haemolysis pilot study was carried out on a selection of quarry dust samples, from each magma type (raw and processed) along with one volcanic ash and one non-volcanic comparison. As some samples (notably, TP04 and 05, FT01 and 03, and PH01 and 02) showed elevated haemolysis, the most haemolytic samples (FT and PH) were repeated and further analyses were also carried out on a broader range of samples, which were selected on the basis of the content of respirable material and, where applicable, the amount of crystalline silica.

A further haemolysis study was conducted on the tumbler-separated PM10 fraction for a range of samples including those which exhibited the greatest haemolytic response and also (as a comparison) several samples which did not exhibit elevated toxicity, representing a variety of magma types. Tumbling at a high rotation speed may cause particles to abrade each other's surfaces upon impact (potentially leading to increased reactivity which can accompany freshened surfaces); to ameliorate this the drum rotation speed was set to the slowest setting. These samples were also lightly re-ground (to freshen surfaces whilst avoiding a reduction in grain size) and the haemolysis assay was repeated to compare freshly created dust with dust that has remained in the quarry environment.

Volcanic Ash Samples

A variety of volcanic ash samples were chosen for surface reactivity tests, to reflect a range of eruption conditions and a spectrum of magma types. Mafic samples are known to provoke a stronger response in terms of iron release and hydroxyl radical production; therefore, the number of samples of mafic ash selected was chosen so as to reflect this. The mafic ash samples chosen represent a range of eruptive styles, reflected in their grain size distributions, from those exhibiting low explosivity such as Vulcanian or Strombolian eruptions (e.g. Etna 2002, Cerro Negro 1995, Vesuvius 1872) to those exhibiting high explosivity as demonstrated by violent Strombolian or sub-Plinian styles (e.g. Vesuvius 1906, Fuego 1974) (Horwell, 2007). The low explosivity eruptive styles generally produce coarser ash which is comparable to the quarry dust produced during processing or in the stockpile of mafic samples; whereas the fine ash from highly explosive eruptions is more akin to the fine grained dust produced during the drilling of mafic quarried samples (as illustrated in Chapter 4 Figure 4.10).

Four samples of intermediate volcanic ash were also selected from Soufrière Hills volcano, two each from two different eruptive styles. Two are from dome collapse events and directly comparable to previously published data (Horwell *et al.*, 2003a) (the same samples were used) and two from ash venting episodes which occurred during the field campaign when the quarried samples were obtained. Both dome collapse and ash venting episodes (in the presence of a dome) usually generate ash with substantial cristobalite (>7 wt. %) (Horwell *et al.*, 2014). Results in this study revealed a total crystalline silica content of 13.5 - 16.4 wt % for dome collapse events in 1999 and 2003 (see Table 4.4 in Chapter 4) and therefore represent the most potentially-hazardous samples from the current eruption.

Fewer felsic samples were analysed due to their exhibiting slightly reduced reactivity (reflected in previously published data (Horwell *et al.*, 2007, Horwell *et al.*, 2010b)) in comparison to intermediate samples and significantly reduced reactivity in comparison to mafic ones. One sample of felsic ash was selected for comparison, from the 2008 explosive, rhyolitic eruption of Chaitén, Chile. Rhyolitic eruptions are rare and this sample, which preceded the dome-forming stage of the eruption, has previously exhibited low radical generation despite increased iron content in comparison with the three other samples analysed from that eruption (Horwell *et al.*, 2008). It is postulated that this is due to the sample's differing composition as a result of the incorporation of hydrothermally altered minerals and is, therefore, more comparable to the weathered quarry samples (Horwell *et al.*, 2008).

For the haemolysis experiments one sample of each magma type was chosen. Volcanic ash samples have never elicited a strong haemolytic response for human erythrocytes (Damby *et al.*, 2013, Hillman *et al.*, 2012, Horwell *et al.*, 2013) and so an extensive selection of these was not included.

Non-Volcanic Quarry Samples

Non-volcanic quarried material has also been included for comparison, including greywacke dust samples of both raw and finished product, and raw and processed sandstone. The PM10 separated fraction of three samples of non-volcanic quarry dust

(representing both sandstone and greywacke) were used in further haemolysis studies as a comparison with the volcanic quarry dust.

Details of sample names and types and which analyses they were subjected to are presented in Table 5.1.

Standards

Two standards were used in experiments as health-pertinent comparisons; quartz as a high toxicity positive control because it is the mineral of primary health concern and TiO_2 as a low toxicity negative control.

Quartz toxicity is variable (Donaldson & Borm, 1998, IARC, 1997) with considerable differences between workplace quartz and that used in experimental studies such as Min-U-Sil or DQ12 (Clouter *et al.*, 2001). DQ12 was established as an international reference sample for experimental work in 1970, with a <5 μm fraction separated by centrifugation from the original <60 μm ground product (Robock, 1973). The material is composed of 87% crystalline silica (as α-quartz) and the remainder is amorphous SiO_2 with small contaminations of kaolinite; with a surface area reported as ranging from 7.4 m^2/g (Robock, 1973) to 10.1 m^2/g (Clouter *et al.*, 2001) both determined by the BET method of N_2 adsorption. A study by Clouter et al. (2001) found that although DQ12 had more ability to cause prolonged inflammation than 2 workplace quartz samples of similar crystalline silica purity, it remained the best *in vitro* predictor for *in vivo* activity in the haemolysis assay. DQ12 was therefore chosen as the quartz positive control for haemolysis experiments.

Min-U-Sil is another experimental standard of quartz commonly used in a variety of toxicological assays relating to respiratory hazard (IARC, 1997, Rice, 2000). It is a finely milled (<5 μm, <10 μm varieties) quartz composed of 99.3 % SiO_2 with very minor impurities of Al_2O_3, K_2O and Fe_2O_3 (<0.3 %) from Mill Creek quarry, Oklahoma (US Silica, 2013). This standard is typically used in analyses of free radical generation by natural mineral particles, including volcanic ash (Damby *et al.*, 2013, Ghiazza *et al.*, 2013, Hillman *et al.*, 2012, Horwell *et al.*, 2003b, Horwell *et al.*, 2010b, Le Blond *et al.*, 2010) and was therefore selected for free radical generation studies here, in order to aid comparability with previously published work.

TiO_2 is also regularly used in experimental studies as a negative control and often when assessing potential toxicity of volcanic ash through haemolysis (Damby *et al.*, 2013, Hillman, 2010, Horwell *et al.*, 2013, Wilson *et al.*, 2000). Aisaka et al. (2008) found that different TiO_2 polymorphs exhibited different levels of haemolytic activity; with rutile (of <5000 nm particle size) less haemolytic than anatase (of either <5µm or <0.025µm). Amorphous TiO_2 (<0.05 µm) was found to be the least haemolytic (Aisaka *et al.*, 2008); however, rutile was selected as the standard for use in this chapter for ease of comparability with other studies which mostly utilise rutile as their negative control.

Table 5.1 Sample types and the analyses conducted upon them (<1mm size fraction).

Volcanic Quarry Dusts					Analyses Conducted			
Magma Category	**Country**	**Quarry**	**Sample Type**	**Sample Name**	**EPR**	**Fe Release**	**Lipid-peroxidation**	**Haemolysis**
Mafic	New Zealand	Bombay	Fines caught from drillers exhaust	BY_01	√	√	√	√
		Flat Top	Drilled fines	FT_01	√	√	√	√
			Finished product (0-25 mm)	FT_03	√	√	√	√
		Puketutu	Drilled fines	P2_01	√	√	√	√
			Drilled fines	P2_05	√	√	-	√
Intermediate	Montserrat	Little Bay	Dust from side of processor	PH_01	√	√	-	√
			Finest grade material	PH_02	√	√	-	√
		Belham Valley	Dust off processor	BV_01	√	√	-	√
			Finished product	BV_03	√	√	-	√
		Trants	Finished product	JN_01	√	√	-	√
			Finished product (0-6mm)	ED_02	√	√	-	√
Felsic	New Zealand	Te Puke	Finished product (0-4 mm)	TP_04	√	√	-	-
			Raw material (quarry wall, ash layer)	TP_05	√	√	-	-
		Henderson	Dust from floor of collection area	Obs_01	-	-	-	√
			Dust from quarry floor outside break hut	Obs_04	-	-	-	√
	Greece	Yali	Finished product (0-1.2 mm)	AP_02	√	√	-	√
			Raw material	LA_02	√	√	-	√
	*U.K.	Brt. Gypsum	Greek perlite expanded in the UK	BGEP	-	√	-	-
Volcanic Ash Samples					**Analyses Conducted**			
Magma Category	**Country**	**Volcano**	**Eruption Type**	**Sample Name**	**EPR**	**Fe Release**	**Lipid-peroxidation**	**Haemolysis**
Mafic	Nicaragua	Cerro Negro	Strombolian-vulcanian eruption (1995)	CerNeg	√	√	-	-
	Italy	Etna	Strombolian eruption (2002)	Etna	√	√	-	√
		Vesuvius	Effusive strombolian eruption (1872)	V1872	√	√	-	-
			Violent strombolian eruption (1906)	V1906	√	√	-	-
	Guatemala	Fuego	Sub-plinian eruption (1974)	Fuego	√	√	-	-

Volcanic Ash (continued)					Analyses Conducted			
Magma Category	**Country**	**Volcano**	**Eruption Type**	**Sample Name**	EPR	**Fe Release**	**Lipid-peroxidation**	**Haemolysis**
Intermediate	Montserrat	Soufrière Hills	Dome collapse (1999)	Mon_99	√	√		
			Dome collapse (2003)	Mon_03	√	√	-	-
			Ash venting eruption (2010)	MA_23	√	√	-	-
			Ash venting eruption (2010)	MA_28	√	√	-	√
	Philippines	Pinatubo	Plinian eruption (1991)	Pina	√	√	-	-
Felsic	Chile	Chaitén	Explosive eruption (2008)	Chai_02	√	√	-	-
Non-Volcanic Quarry Dusts					**Analyses Conducted**			
Rock Type	**Country**	**Quarry**	**Sample Type**	**Sample Name**	**EPR**	**Fe Release**	**Lipid-peroxidation**	**Haemolysis**
Greywacke	New Zealand	Hunua	Finished product (0-5 mm)	HU_01	√	√	-	-
			Backbreak fracture ("Waitamata Ash")	HU_04	√	√	-	-
Sandstone	UK	Moneystone	Raw sandstone	MSR	√	√	-	-
			Processed cristobalite	MSC	√	-	-	-
Standard Comparisons					**Analyses Conducted**			
Type			**Mineral**	**Sample Name**	**EPR**	**Fe Release**	**Lipid-peroxidation**	**Haemolysis**
Positive			Quartz	MinUsil	√	√	-	-
			Quartz	DQ12	-	-	-	√
Negative			Rutile	TiO_2	-	-	-	√

Key: **√** = analysis carried out as part of this study; **o** = sample data obtained from previously published research; **-** = sample not analysed. BET = Brunauer Emmett Teller method of gas adsorption, EPR = Electron Paramagnetic Resonance Spectroscopy, *Sample of Greek perlite expanded in UK by British Gypsum.

5.3.3 Free Radical Generation in the <1mm fraction

Background

The potential for dust to generate free radicals in the lung can be measured using Electron Paramagnetic Resonance Spectroscopy (EPR), which is also known as Electron Spin Resonance Spectroscopy (ESR). This is a technique which allows for the quantification of unpaired electrons (e.g. free radicals). In an atom, electrons spin along their orbit around the nucleus (Gerson & Huber, 2003, Sing, 1982). This spin leads to a 'magnetic moment' which, in the presence of an external magnetic field, will align itself either parallel or perpendicular to the magnetic field. Both of these alignments have specific energies (lower and higher respectively) with the exact difference depending upon the surrounding electrons. The splitting of these energy levels is directly proportional to the strength of the magnetic field applied and characterised as the electron's g-factor. When the electromagnetic radiation applied (in the form of microwave) is at a frequency equal to the separation between the energies, the energy from the applied magnetic field will be absorbed. This absorption is detected and displayed in the form of a spectrum. Splitting of the spectral line into several components (known as the Zeeman effect) is controlled by the distance between the radical and the nucleus (Atherton, 1993, Gerson & Huber, 2003). The amplitude of the peaks along the spectral line is directly proportional to the quantity of radicals measured.

Analysis

The analysis was conducted using hydrogen peroxide in order to replicate the iron-catalysed surface reactivity of the Fenton reaction (reaction 4 in Reaction 5.1) which leads to the production of the hydroxyl free radical. 150 mg of dust sample (of the <1mm size fraction) was weighed into a darkened glass bottle and 500 µl of phosphate buffer (0.5 M) was added in order to maintain a constant pH of 7.4 (identical to lung fluid). Most free radicals have a half-life of only 0.001 s, making direct detection impossible. A 'spin-trapping' agent was also added in order to trap the radicals, making them stable for measurement, in the form of 250 µl of 5,5'-dimethyl-1-pyrroline-N-oxide (DMPO) which had been purified by carbon filtration. Finally, 500 µl of H_2O_2 was

added and the sample placed upon a magnetic stirring plate. The sample was analysed after 10, 30 and 60 minutes by syringing through a 0.45 µm cellulose filter into a 50 µl capillary tube. The sample was analysed in a Magnettech Miniscope 100 MS EPR spectrometer working at 10 mW microwave power, 10 dB attenuation and modulation amplitude of 1G. Two scans of 80 sec. each were taken. An example of the spectrum generated is presented in Figure 5.2, where the four central peaks represent HO• radical release and the two outer peaks are generated by the Mn^{2+} standard.

The integrated amplitude of the peaks generated is proportional to the quantity of radicals produced with the number of radicals typically calculated by including a solid solution of Mn^{2+} in $CaCO_3$ as a calibration standard. The Mn^{2+} standard is no longer used in the lab at the Università degli Studi di Torino. Therefore, in recent work by our group, an average of the last run Mn^{2+} standard has been used (Horwell *et al.*, 2013) in order to integrate the radical peaks for quantification, thereby allowing comparison with formerly published data.

The surface reactivity data have been adjusted for surface area (data in Chapter 4) and each sample was run 3-5 times.

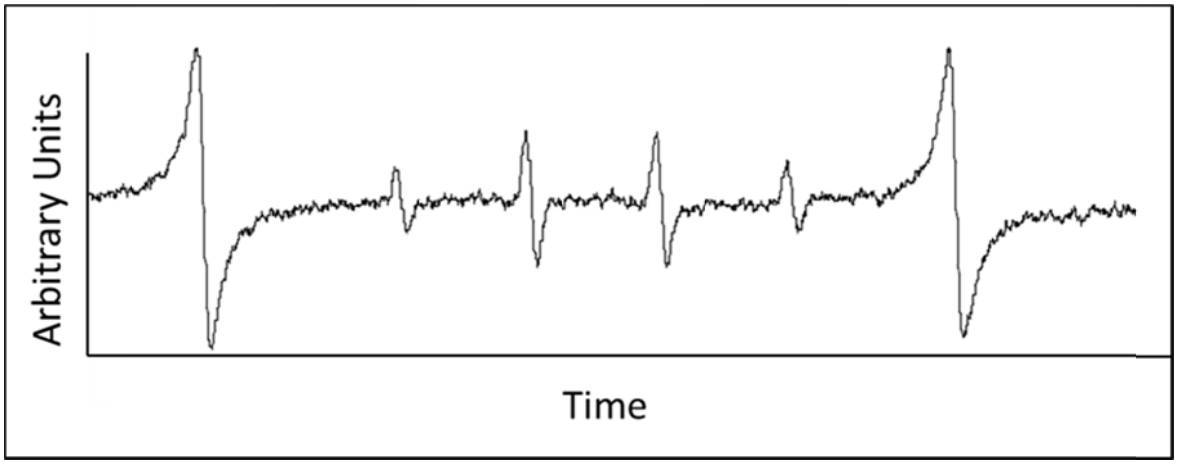


Figure 5.2 A typical EPR spectrum showing HO• radical release (four central peaks) and the Mn^{2+} standard (two outer peaks). The amplitude of the peaks is measured in arbitrary units.

5.3.4 Iron Release in the <1mm size fraction

Background

Naturally occurring molecules in the lung can act as chelators for iron on the surface of dust particles, removing them from the particle surface. As outlined in the Haber-Weiss cycle (Reaction 5.1 above) both di- and tri-valent iron ions are implicated in the production of hydroxyl free radicals. The quantity of removable di- and tri-valent iron on dust particle surfaces was measured in the presence of ferrozine, a bidentate N donor chelator (pH 4), specific to Fe^{2+} and, in a separate test, with the addition of ascorbic acid which reduces trivalent iron to divalent iron. Thereby, both divalent and total iron were measured and the quantity of trivalent iron was obtained by subtracting divalent from total. The resulting solutions were analysed spectrophotometrically as ferrozine forms a coloured complex with Fe^{2+}.

Analysis

Two sets of 10 mg of each dust sample (<1mm size fraction) were weighed out into tubes. To the first set, 5 ml of ferrozine (1 mMol) and 5 ml ascorbate (6 mMol) were added. To the second set, 5 ml of ferrozine and 5 ml bi-distilled water were added. Two control solutions, in which dust was absent, were also made up. The solutions were then placed in an incubating shaker set at 37 °C (body temperature). At approximately the same time each day, 1.5 ml of solution was removed from each tube and placed into an eppendorf centrifuge tube. These were centrifuged for 15 min. and then the top 1 ml was removed and placed into a cuvette for analysis. Where the solution had visibly turned dark purple, it was diluted with milli-q water. Any undiluted sample was returned to the original tube and incubated. Measurements were taken every 24 hours for days: 1, 2, 3, 4, 7, 8 and 9 (access to lab was not possible at weekends) except for the felsic and non-volcanic samples where data for day 3 is missing due to a public holiday when the lab was closed. The samples were analysed using an Uvikon 930 dual beam spectrophotometer (Kontron Instrument) with the following parameters: wavelength 562 nm, EmM: 27.9 mM/cm.

The iron release data are normalised to surface area with dilution also accounted for, and each sample was run in duplicate, aside from the mafic ash and quarry samples

which were run in triplicate (as they are known to release more Fe than their intermediate and felsic counterparts) on separate subsamples. Calibration of both ferrozine and ferrozine with ascorbic acid was run to account for lamp degradation using three solutions: (i) a 1 mM solution of ferrozine and H2O, ii) a 1mM solution of ferrozine and ascorbic acid and iii) a 1 mM solution of Cl_2Fe4H_2O, at 20 different concentrations; the gradient of the calibration curve was determined as 27.9 (molar extinction coefficient) and factored into analyses.

5.3.5 Haemolysis in the <1mm and <10μm fractions

Background

There exists a suite of *in vitro* toxicity tests for assessing the pathogenic response of natural mineral particles. It was beyond the scope of study to carry out a full toxicity investigation; however, the haemolysis assay (involving incubating particulate with red blood cells) has been conducted on a suite of samples. Whilst there are no erythrocytes in the lung, this assay is a good indicator of the ability of particulates to induce membrane damage and is often used to indicate the potential cytotoxicity of quartz-containing mineral dusts (Vallyathan *et al.*, 1983, Wilson *et al.*, 2000). A variety of ash samples from historical eruptions have been tested using ovine or bovine erythrocytes (Vallyathan *et al.*, 1983, Wilson *et al.*, 2000). Since 2008, haemolysis using human blood cells has been carried out on a suite of volcanic ash samples (from volcanoes including Rabaul (Papua New Guinea)(Le Blond *et al.*, 2010), Merapi (Indonesia)(Damby *et al.*, 2013), Sakurajima (Japan)(Hillman *et al.*, 2012), Soufrière Hills volcano (Montserrat)(Baxter *et al.*, 2014) Eyjafjallajökull and Grímsvötn (Iceland) (Horwell *et al.*, 2013) and Mt St Helens (USA) (Damby, 2012) and results have been uniformly negative, being close to data for the negative control, TiO_2. The results of these studies are discussed in greater detail in Chapter 2 Section 2.3.2. Human erythrocytes were used in this study, obtained from a donor within the ethical framework of the Centre for Inflammation Research at the University of Edinburgh.

All samples were run in triplicate (three plates) and each sample was run in triplicate on each plate. DQ12 (a quartz standard) was used as a positive comparison as it exhibits greater reactivity than industrial quartz samples (Duffin *et al.*, 2001) and rutile (a TiO2 polymorph) was used as the negative comparison. Each plate was also run with the cell-lysing surfactant Triton-X (0.1 %) as a positive control and pure saline solution as a negative control.

Analysis

40 ml of fresh venous blood was collected from a human donor and added to a 3.8 % citrate solution in order to prevent coagulation. The blood was gently inverted and centrifuged at 2000 rpm for 10 minutes. The supernatant was removed, leaving behind 85 % haemocrit (volume % erythrocytes). The packed red blood cells were added to 13 ml of buffer (0.428 g $NaHCO_3$ 30 mM; 0.386 g $NaHPO_4$ 16 mM; 3.360 g Dextrose/D-glucose 110 mM; 1.7 g mannitol 55 mM) which was diluted in 170 ml dH_2O. For each 96-well flat bottomed plate run, 1 ml of red blood cells were washed with saline by centrifuging at 4000 rpm for 5 minutes, 3 times. Then 400 µl of washed red blood cell suspension was added to 7.6 ml saline (i.e. 5 % by volume of red blood cell solution in saline).

Dust samples were weighed out and suspended in saline at a concentration of 1 mg/ml and sonicated in a water bath for 10 minutes. The samples were then further diluted with NaCl so that for each sample there were 6 concentrations: 1, 0.5, 0.25, 0.125, 0.0625 and 0.0312 mg/ml. 150 µl of particle solution (of each concentration) was added in triplicate to wells in the plate. 75 µl of red blood cell suspension was then added to each well and gently mixed by pipetting. The plate was incubated at room temperature for 30 minutes with gentle shaking. The plate was then centrifuged at 2500 rpm for 5 minutes. 75 µl of solution was removed from the upper layer of solution in each well (carefully, so as not to disturb the layer of blood cells on the bottom) and transferred to a new plate. Any bubbles were dispersed by blowing air over the plate and it was then placed into the plate reader. The absorbency of the wells was read at a wavelength of 550 nm (the wavelength for haemoglobin) and the

optical density obtained using Gen 5 software. The haemolytic activity of the samples run was calculated as a percentage by using the equation of a straight line (y=mx+b):

$$\%\ Haemolysis\ (x) = [optical\ density\ (y) - negative\ control\ optical\ density\ (b)]\ /\ [(positive\ control\ optical\ density - negative\ control\ optical\ density)/100]\ (m)$$

Equation 5.1

Samples for the in-depth (post pilot) study were split into two groups; the red blood cells were freshly collected prior to the start of experiments for group 1 and were 48 hours old when group 2 experiments began; they were stored in refrigerated conditions when not in use. Blood cells are viable for the haemolysis assay for up to 2 weeks after collection; however, they become more fragile over time which means that samples analysed soon after collection will yield a smaller haemolytic response than they would several days later. To account for this increase in fragility each sample and standard was analysed three times, with each run (on a separate subsample) occurring at the beginning, middle and end of the analysis period. This yields larger errors due to the difference between individual runs, but presents a more accurate average for comparison among samples and standards. A blank plate (samples without blood cells) was also run for all of the samples to ensure that any leaching of red-coloured minerals (e.g. oxidised iron) by the saline would not affect the absorbency reading. Optical density (OD) was read at 550 nm using a Synergy HT microplate reader (BioTek Instruments, Inc. VT, USA) with a measurement range of 0.000 to 4.000 optical OD, and accuracy and repeatability of 0.000 to 2.000 OD +/- 1.0%, the optics range is 200-999nm with accuracy +/-2nm and repeatability of +/- 0.2nm.

5.3.6 Detection of secondary clay phases

Background

Those samples which gave an elevated haemolytic response were all from comparatively ancient deposits and were further investigated for clays which might influence the haemolytic potential of the samples. The clay fraction was isolated in an attempt to qualitatively identify the phases present by XRD (further details of the XRD theory are presented in the Methodology section of Chapter 4).

Four of these samples were also made into resin blocks (as described in Chapter4) which allowed observation of the cross section of minerals by SEM-EDS.

Analysis

Separation of the clay fraction was conducted by incubating the sample with a peptisation solution (as a de-flocculant) and distilled water and drying on a glass slide as per established methodology for clay samples (Velde, 1992). Following several rounds of centrifugation and removal of the non-clay fraction, the remaining clay fraction was pipetted onto glass slides and dried for 48 hours. The slides were then run by XRD (on a Bruker AXS D8 Advance with DAVINCI design at the Department of Chemistry, Durham University) and attempts made to match the resulting patterns with a library of standards.

SEM-EDS analysis was conducted on samples mounted in resin, polished and observed in cross-section using a Hitachi SU-70 FEG SEM equipped with Oxford Instruments INCA analysis system (EDS) at the GJ Russell Microscopy Facility, Department of Physics, Durham University.

5.3.7 Statistical Analyses

Statistical analyses were conducted using GraphPad PRISM software (San Diego, California). An unpaired 2-tail Welch's t-test was selected to compare the significance of differences in two-sample comparisons. The ANOVA one-way variance test was used to determine significance with multiple comparisons, the Tukey post-test was also run (for multiple comparisons between sample means). In all cases, results were considered significant when $p<0.05$.

5.4 Results

The results are presented in two sets of summary tables and also discussed individually by technique.

Table 5.2 – Results Overview: The EPR data for 30 min (data for 10 min and 60 min are presented in Appendix III) and Fe-release data for day 7 (data for days 1-9 are presented in Appendix III) for a range of volcanic quarry dust, volcanic ash and non-volcanic quarry dust samples. Fe^{3+} data are the difference between the total iron and the Fe^{2+} data.

Volcanic Quarry Dusts			Results							
Country	Quarry	Sample Name	EPR 30 min (µmol/m²)		Fe Release Day 7 (µmol/m²)					
			Mean	Error (3σ)	Fe^{2+} Mean	Error (3σ)	Fe^{3+}	Error (3σ)	Total Fe	Error (3σ)	Fe^{2+}/Fe^{3+}
New Zealand	Bombay	BY_01	0.31	0.30	19.59	1.01	23.73	6.86	43.32	7.47	0.83
	Flat Top	FT_01	0.08	0.04	16.56	1.75	17.95	10.30	34.51	10.36	0.92
		FT_03	0.04	0.01	10.41	5.32	16.42	7.51	26.83	11.35	0.63
	Puketutu	P2_02	0.30	0.00	8.38	4.23	41.79	29.17	50.17	33.10	0.20
		P2_05	0.36	0.17	35.81	7.40	97.77	51.54	133.58	50.64	0.37
Montserrat	Little Bay	PH_01	0.20	0.09	9.19	2.85	17.94	6.07	27.13	3.21	0.51
		PH_02	0.05	0.06	4.29	1.89	7.20	2.81	11.49	0.92	0.59
	Belham Valley	BV_01	0.24	0.30	3.55	2.25	15.51	10.96	19.06	8.7	0.23
		BV_03	0.19	0.27	2.67	2.00	19.62	4.94	22.29	7.8	0.14
	Trants	JN_01	0.79	0.01	2.36	2.00	16.47	4.88	18.83	2.88	0.14
		ED_02	0.38	0.37	3.29	1.64	22.70	22.24	25.99	20.59	0.15
New Zealand	Te Puke	TP_04	0.03	0.00	0.34	0.13	3.02	0.16	3.36	0.03	0.11
		TP_05	0.04	0.00	0.64	0.25	4.44	2.01	5.08	1.76	0.14
Greece	Yali	AP_02	0.08	0.12	0.24	0.41	0.84	0.47	1.09	0.88	0.29
		LA_01	0.15	0.07	-	-	-		-	-	-
Greece	British Gypsum	BGRP	0.07	0.01	-	-	-		-	-	-
		BGEP	0.06	0.04	2.25	0.13	0.91	1.00	2.58	0.37	6.69

Volcanic Ash				Results								
Magma Category	Country	Volcano	Sample Name	EPR 30 min								
				Mean	Error (3σ)	Fe^{2+} Mean	Error (3σ)	Fe^{3+}	Error (3σ)	Total Fe Mean	Error (3σ)	Fe^{2+}/Fe^{3+}
Mafic	Nicaragua	Cerro Negro	CerNeg	1.68	1.28	98.55	1.87	137.05	13.50	235.60	15.37	0.72
	Italy	Etna	Etna	5.78	3.10	114.34	43.18	362.23	189.89	476.57	146.71	0.32
		Vesuvius	V1872	1.23	0.22	153.45	49.54	177.43	123.53	330.88	73.99	0.86
			V1906	1.42	0.20	5.09	4.66	32.18	0.03	37.27	4.69	0.16
	Guatemala	Fuego	Fuego	0.66	0.50	50.01	13.31	131.87	34.95	181.88	21.64	0.38
Intermediate	Montserrat	Soufrière Hills	MA_23	1.58	0.32	3.93	0.34	13.02	0.79	16.95	1.13	0.30
			MA_28	1.89	0.07	2.68	0.84	47.21	38.31	49.89	37.47	0.06
			Mon_99	0.67	0.23	2.90	0.09	18.07	3.21	20.96	3.12	0.16
			Mon_03	0.84	0.51	5.96	0.04	18.75	0.50	24.71	0.45	0.32
	Philippines	Pinatubo	Pina	0.26	0.05	12.90	1.04	17.07	2.50	29.97	3.54	0.76
Felsic	Chile	Chaitén	Chai_02	0.36	0.09	35.33	24.61	16.12	21.55‡	51.45	3.06	2.19
Non-Volcanic Quarry Dusts				**Results**								
Magma Category	Country	Quarry	Sample Name	EPR 30 min								
				Mean	Error (3σ)	Fe^{2+} Mean	Error (3σ)	Fe^{3+}	Error (3σ)	Total Fe Mean	St. Error	Fe^{2+}/Fe^{3+}
Greywacke	New Zealand	Hunua	HU_01	0.11	0.02	30.84	1.95	10.94	2.18	41.77	6.10	2.82
			HU_04	-	-	14.85	1.46	5.89	7.61	20.74	1.40	2.52
Sandstone	UK	Moneystone	MSR	1.21	0.76	2.02	1.90	12.72	9.23	14.74	1.19	0.16
			MSC	0.08	0.04	-	-	-	-	-	-	-

5.4.1 Free Radical Generation in the <1mm size fraction

During the hydroxyl radical generation tests, a spectrum is generated by the EPR spectrometer to represent the quantity of hydroxyl radicals produced; all spectra appear in the form shown in Figure 5.2 with the intensity of the peak (peak height) varying according to number of radicals generated. The data are presented here in three formats: first, the number of radicals generated after 30 minutes (average of three runs) is shown in the overview table (5.2), secondly in graphs which show the kinetics of the reactions (average of 3 runs) over the full 60 minutes of each experiment (Figure 5.4); and thirdly, as a graph which plots hydroxyl radical generation at 30 minutes against total iron released after 7 days (Figure 5.6). The parameters in this plot were chosen as several papers on the hydroxyl radical generation in volcanic ash have used this format (Damby *et al.*, 2013, Horwell *et al.*, 2013, Horwell *et al.*, 2007, Horwell *et al.*, 2010a, Le Blond *et al.*, 2010). Horwell et al. (2007) first used this format having determined that HO• generation data at 10 min. were not representative of the full experiment as HO• were still being generated after this time, but that by 60 min., the 'spin trap' (DMPO) may be exhausted, thereby further generation of radicals may not be stabilised for measurement by the EPR spectrometer. Therefore, 30 min. was chosen as the best parameter and has been used here. Likewise, Horwell et al. 2007 also determined, by analysing Fe release graphs such as Figs. 5.7-5.13 that, by day 7, iron release had often stabilised. There is merit in analysing for up to 9 or 10 days instead, when stabilisation is more reliable. The experiments here were run for 9 days, however, in Figure 5.14 the data are presented for day 7 because, by continuing with the format used in previous studies, a direct comparison can be made. Other formats were plotted for this study but did not give results that were considered superior to the existing format, so are not shown here.

For the quarry and ash samples studied, the mafic dusts (Figure 5.4a) were generally more prolific at generating radicals in comparison to the intermediate (Figure 5.4b), felsic (Figure 5.4c) and non-volcanic material (Figure 5.4d); however, this difference was not statistically significant. Volcanic ash consistently generated more radicals than quarried material of the same magma type, with volcanic ash also

exhibiting a much greater variation (range) than quarried dust when comparing within the same magma type. For example in Figure 5.4a, hydroxyl radical generation for mafic volcanic ash at 30 minutes varies from 0.7-5.8 μmol/m^2, whereas mafic quarry dusts range from (virtually) 0.0-0.4 μmol/m^2. In the intermediate ash samples, the variation was again broader (giving a range of 0.7-1.89 μmol/m^2 at 30 min) than the quarried samples (0.05-0.79 μmol/m^2). This illustrates that the most reactive quarry dusts of intermediate magma type are comparable to the less-reactive ash samples of the same magmatic origin. The felsic quarried samples elicited few radicals (0.06-0.15 μmol/m^2) whereas the single felsic ash sample generated 0.36 μmol/m^2 at 30 min; by comparison the basaltic Etna ash sample generated 5.78 μmol/m^2 in the same time frame (note difference in y-axis logarithmic scales in Figure 5.4 a-d). The non-volcanic comparison quarry dusts exhibited a broader range of radical generation than the volcanic quarry dusts (0.08-1.21 μmol/m^2 at 30 min); but not as extensive a range as the volcanic ash samples. All of the controls (shown in Figure 5.4d) exhibited very low radical generation.

Samples reached their peak radical generation at varying times throughout the experiment (measures were taken at 10, 30 and 60 minutes) and there does not appear to be any clear pattern in the data to explain this.

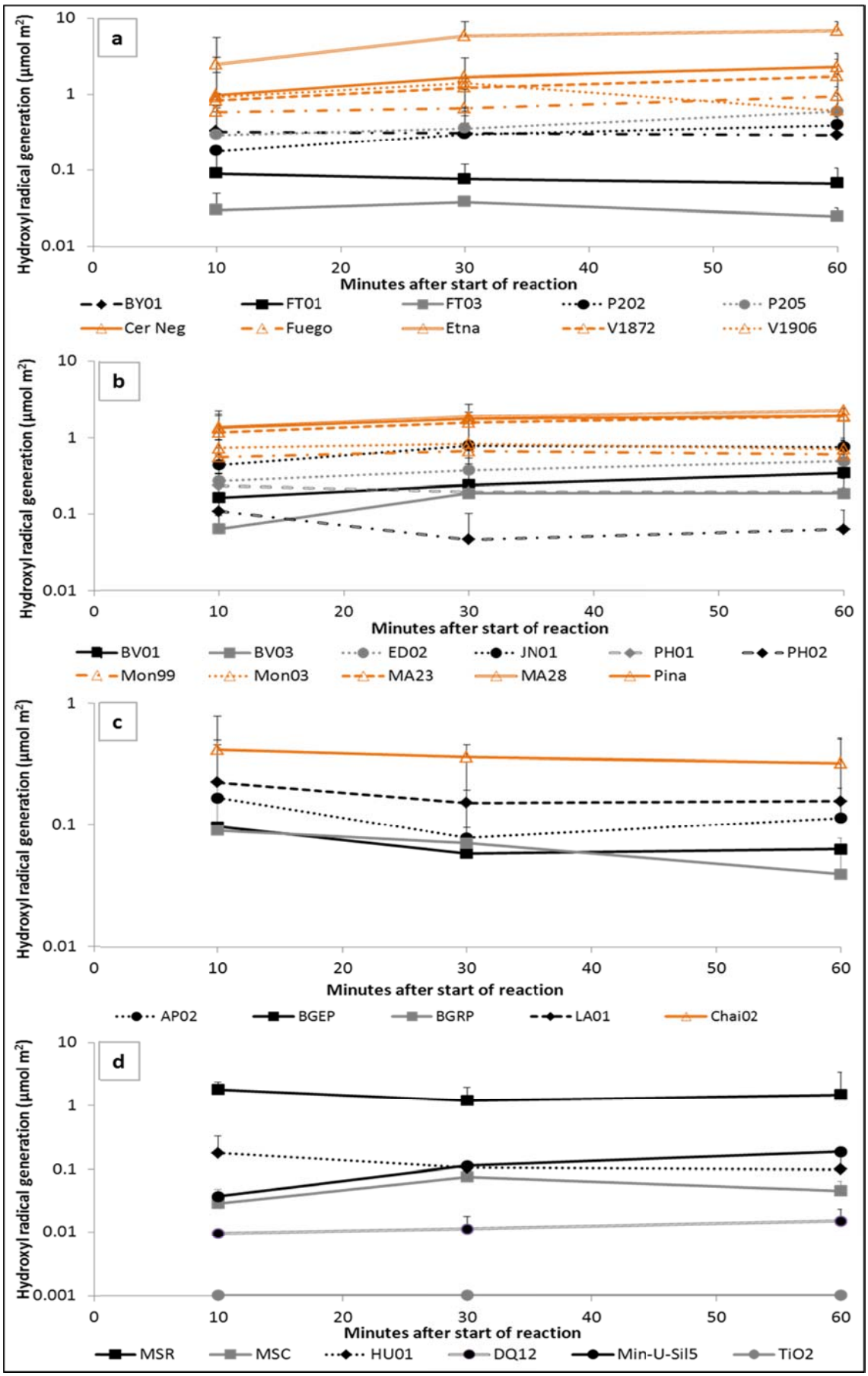


Figure 5.4 Hydroxyl radical generation over 60 minutes for a) mafic, b) intermediate and c) felsic quarry dust (black and grey) and volcanic ash samples (orange), and d) non-volcanic quarry dust and standards. Average of n=3 with error shown to 3σ.

5.4.2 Iron Release in the <1mm size fraction

The iron released by the samples was measured in two ways; Fe^{2+} and total Fe; with the difference calculated to show the contribution of Fe^{3+}. These results are presented in three ways; first, the quantity of iron released (average of three runs for mafic samples and two runs for all others) is shown in the overview table (5.2), secondly in graphs which show the kinetics of the reactions (average of 3 runs) over the full 9 days of each experiment (Figure 5.5); thirdly, as mentioned previously, as a graph which plots hydroxyl radical generation at 30 minutes against total iron released after 7 days (Figure 5.6). The total iron (Fe^{2+} + Fe^{3+}) released over the nine day period is shown in Figure 5.5 a-d and, similarly to the radical generation data, the mafic samples (Figure 5.5a) released greater amounts of total iron from their surfaces than the intermediate (Figures 5.5b), felsic (Figures 5.5c) or non-volcanic samples (Figure 5.5d). Overall, however, volcanic ash released more iron for every magma type than the quarry samples (note difference in the y-axis logarithmic scale between Figure 5.5a and b-d).

All of the quarry dusts had more ferric (Fe^{3+}) than ferrous (Fe^{2+}) iron, revealing that their surfaces had been oxidised (Table 5.2). This difference was considerable for some samples, such as the mafic P2_01 and P2_05 and all of the intermediate samples (PH, BV, JN, ED). The difference was much smaller, however, for samples such as the felsic TP_04 and TP_05, and the mafic BY_01 and FT_01. One sample from Flat Top (FT_01) had almost equal parts of Fe^{2+} and Fe^{3+} whilst the other sample (FT-03) had 1.6 times more Fe^{3+} than Fe^{2+}. All of the volcanic samples also contained more Fe^{3+} than Fe^{2+} (which is in keeping with previous results on these samples (Horwell *et al.*, 2007, Horwell *et al.*, 2003a) with the exception of the Chaitén sample. The non-volcanic comparisons (HU_01 and 04) contained as much as three times more Fe^{2+} than Fe^{3+}. The total iron released by the greywacke (HU_01 and _04), however, was moderate compared with mafic and intermediate samples of quarry dust and ash.

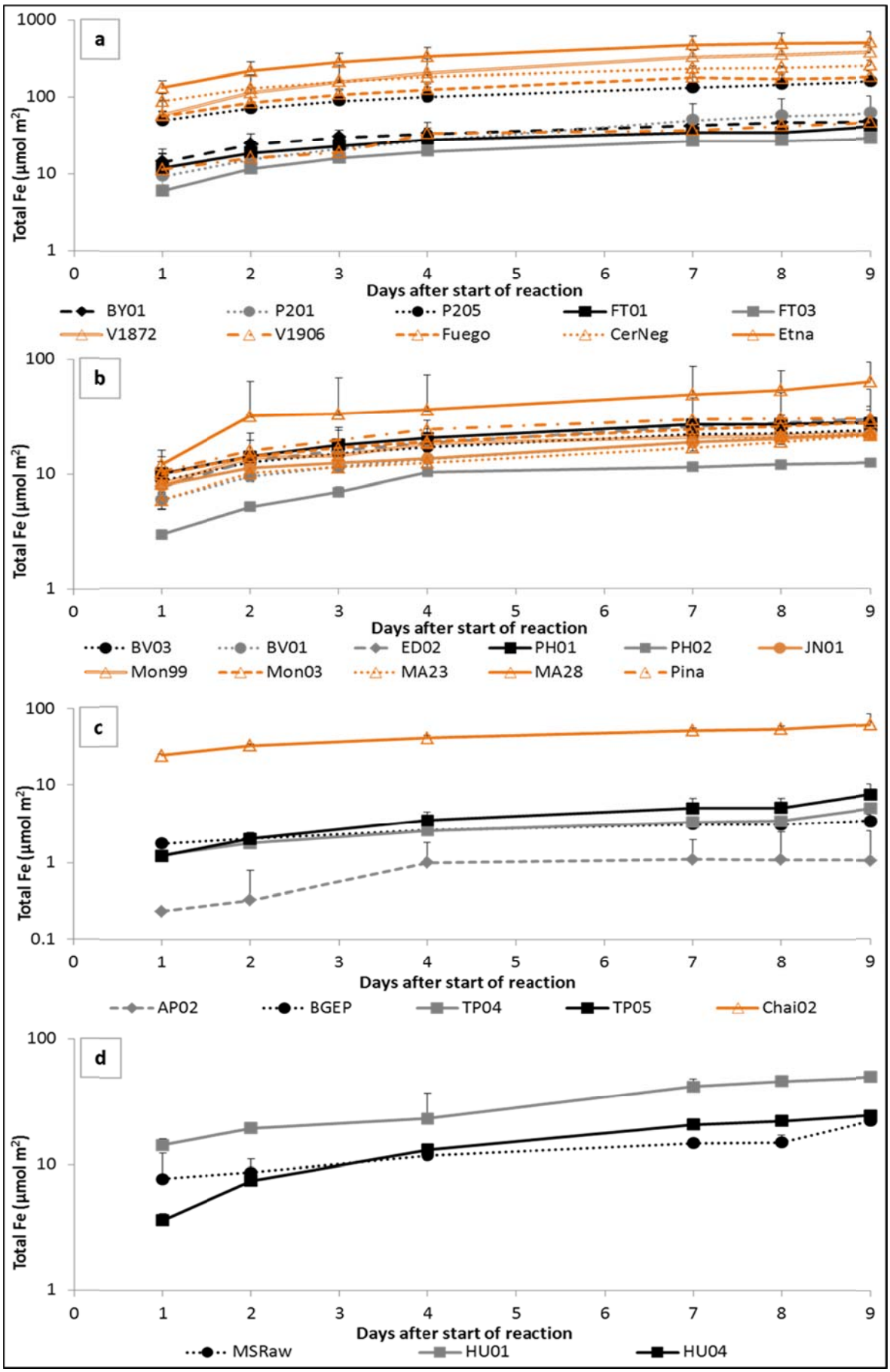


Figure 5.5 Total iron released over 9 days for a) mafic, b) intermediate and c) felsic quarry dust and volcanic ash samples, and d) non-volcanic quarry dust and standards. Average of n=3 with error shown to 3σ.

The radicals generated after 30 min. and total Fe released at 7 days (in the <1mm size fraction) are plotted in Figure 5.6, with the samples grouped by magma type for the quarried material. Comparing the release of iron with the generation of radicals does not reveal a correlation between the amount of iron released and the number of radicals generated. Six of the ash samples generated 1.5-2.0 µmol/m^2 of radicals (MA23, MA28, Pinatubo, Cerro Negro, V1872 and V1906) but their total iron varied from 17-330 µmol/m^2. The same pattern (a range of iron but little difference in radical generation) can be seen in the quarried mafic samples. The andesitic quarried samples, however, all released a comparatively similar amount of total iron (12-27 µmol/m^2) whilst also generating the largest range of radicals 0.05-0.79 µmol/m^2 and a similar pattern can be observed in the andesitic ash samples.

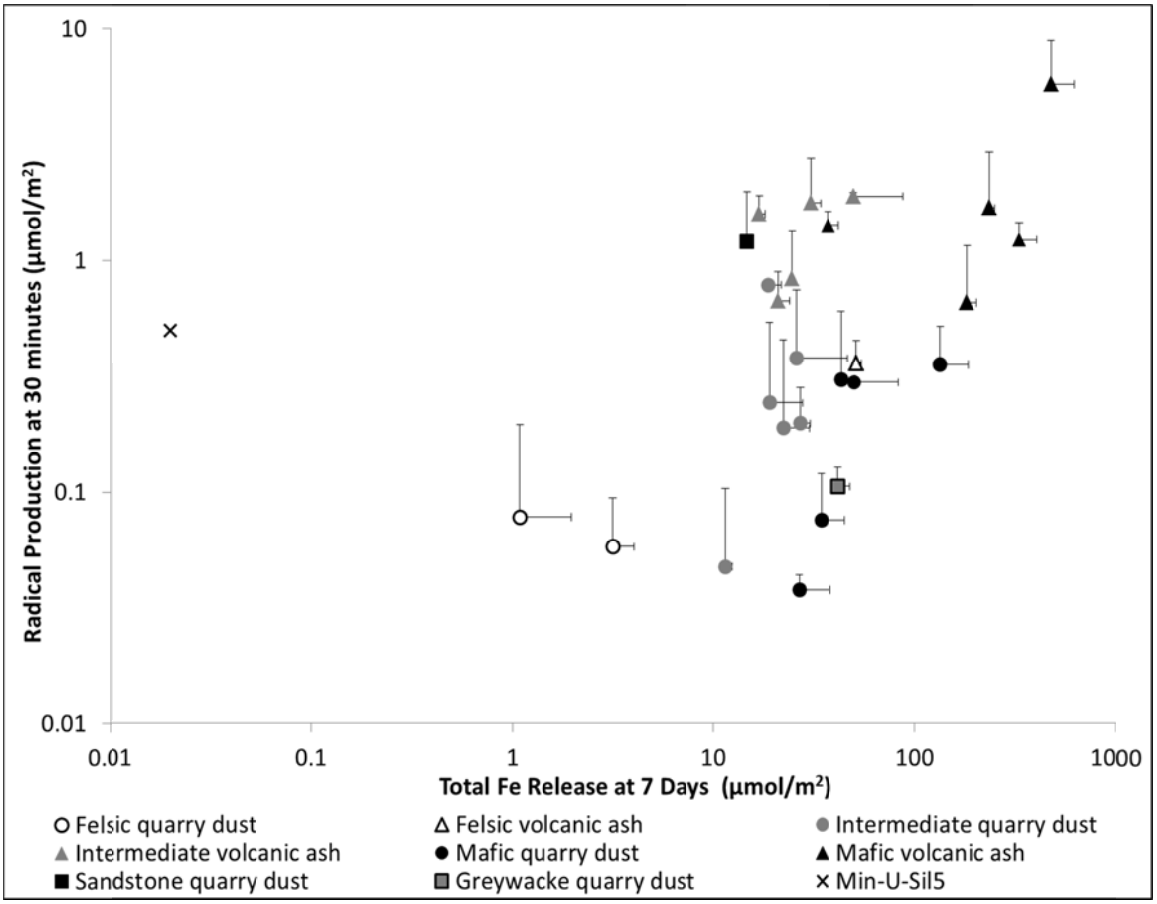
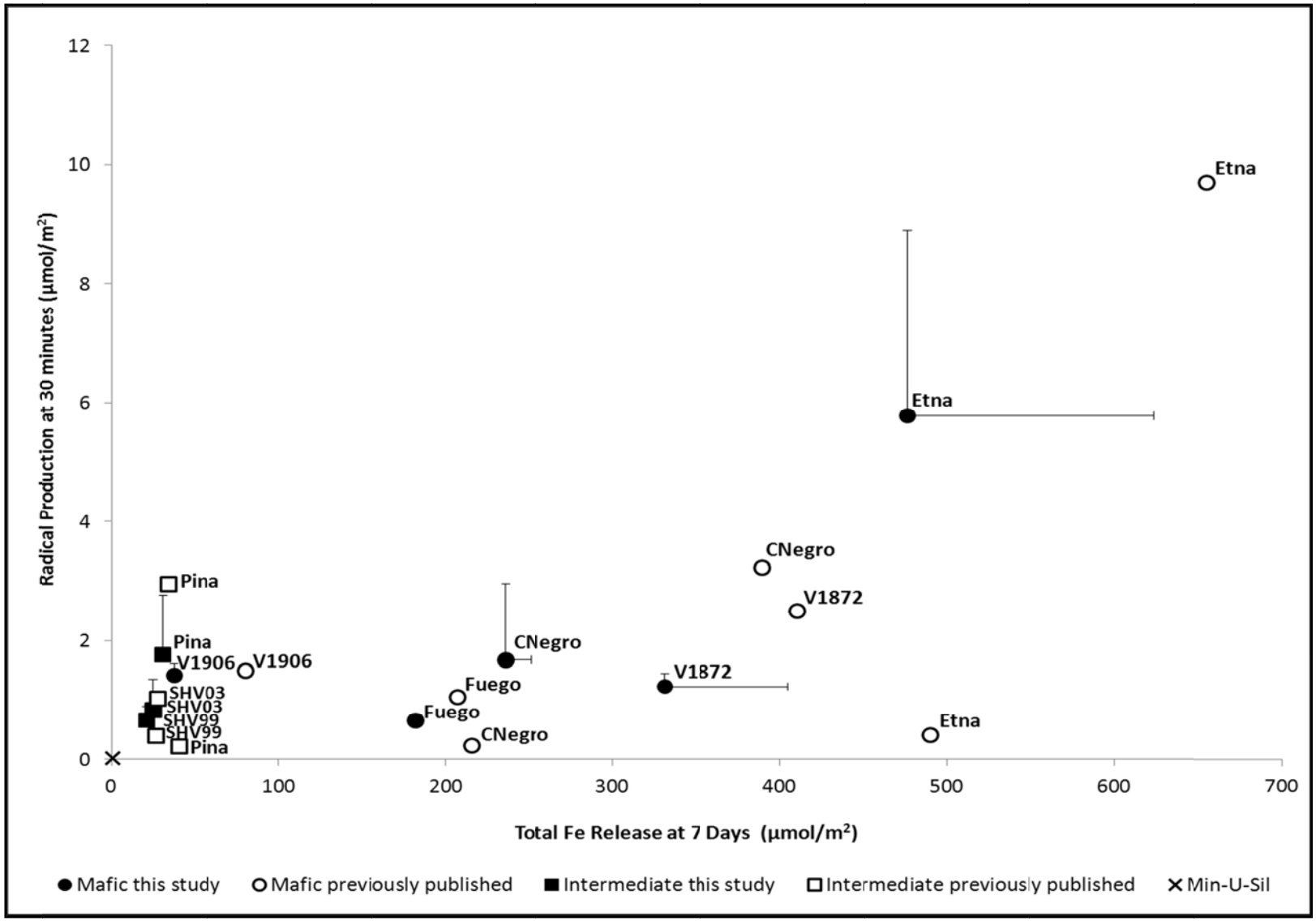


Figure 5.6 Total iron released after 7 days (x-axis) and hydroxyl radical generation after 30 minutes (y-axis) for a range of volcanic quarried samples, non-volcanic quarried samples volcanic ash and quartz control. Average of n=3 with error shown to 3σ.

Figure 5.7 Hydroxyl radical generation at 30 minutes versus total iron mobilised by chelation after 7 days for volcanic ash samples only. Results from this study are shown in black, results from previously published studies conducted on the same samples are shown in white, after: Horwell et al. (2007), Horwell et al. (2010b) and Damby et al. (2013). Pina: Pinatubo; CNegro: Cerro Negro; SHV: Soufriere Hills Volcano (erupted 1999 and 2003); V: Vesuvius (erupted 1872 and 1906).



Previous studies on volcanic ash have shown that some mafic ash generates substantially more radicals and releases more iron for the samples which release high quantities of iron (e.g. Etna), than intermediate or felsic ash (Damby *et al.*, 2013, Horwell *et al.*, 2007, Horwell *et al.*, 2010b). The results presented here show good relative reproducibility with these previous studies. Several of the ash samples analysed here were splits from samples previously analysed and both sets of results are presented in Figure 5.7. Relative to each other, samples present good reproducibility (in terms of comparing the most reactive samples or the least reactive samples); however, individually there is quite a broad margin of error which is likely to result from the variability associated with analysing natural, highly heterogeneous samples.

Mafic and intermediate dusts generated more hydroxyl radicals than felsic quarry dusts and in the iron release the mafic samples released an order of magnitude more Fe than intermediate and felsic dusts. In order to determine whether these differences are statistically significant, a one-way ANOVA with Bonferroni correction was performed for hydroxyl radical production at 10, 30 and 60 mins and for total Fe released on days 7 and 9, shown in Table 5.3. No significant difference was observed between the radical generation of mafic and intermediate or mafic and felsic dusts; however, intermediate dusts released significantly more radicals than felsic dusts at 30 min and 60 min ($p \leq 0.05$). For iron release, there was no significant difference between intermediate and felsic dusts; however, mafic dusts released significantly more iron ($p \leq 0.05$) than both intermediate and felsic dusts.

Table 5.3 Results of a one-way ANOVA with Bonferroni correction performed on the three magmatic groupings for EPR at 10, 30 and 60 mins and for total Fe released on days 7 and 9; ns = non-significant, * p≤0.05 (significant), ** p≤0.01 (very significant), ***p≤0.001 (extremely significant).

	Radical Production			Total Fe released	
Groupings compared	**10 min**	**30 min**	**60 min**	**Day 7**	**Day 9**
Mafic – Intermediate	ns	ns	ns	*	*
Mafic – Felsic	ns	ns	ns	*	*
Intermediate – Felsic	ns	*	*	ns	ns

An unpaired 2-tail Welch's t-test was conducted to compare the significance of differences in radical production and iron release, between mafic quarry dust and mafic volcanic ash for EPR at 10, 30 and 60 min and for total iron released over days 1-9. Drilled and blasted mafic quarry dusts were selected (as they are likely to have the freshest surfaces) versus volcanic ash of a comparable magmatic composition as determined in Chapter 4 by XRF; Vesuvius 1872 as comparable to Puketutu, Etna as comparable to Bombay, and Cerro Negro as comparable to Flat Top as shown in Table 5.4. Overall, the difference between radical production and total iron release was determined as very significant as was total iron on day 7 (total iron on day 9 was found to be extremely significant p≤0.001), indicating that mafic volcanic ash releases more radicals and generates more iron than freshly quarried mafic lavas.

Table 5.4 Results of an unpaired 2-tail Welch's t-test conducted for EPR at 10, 30 and 60 min and for total iron released over days 1-9 on drilled and blasted mafic quarry dust versus ash of a comparable magmatic composition; ns = non-significant, * p≤0.05 (significant), ** p≤0.01 (very significant), ***p≤0.001 (extremely significant).

Mafic Groupings Compared	Radical Production			Total Fe released	
	10m	30m	60m	Day 7	Day 9
Quarry dust versus comparable ash	**	**	**	**	***

A further unpaired 2-tail Welch's t-test was conducted upon the intermediate quarry dust from the Soufrière Hills deposit and erupted ash from the Soufrière Hills volcano. This compared the significance of differences in radical production at 10, 30 and 60 min and for total iron released over days 1-9 as shown in Table 5.5; which revealed that the difference in radical production was 'extremely significant' (p≤0.001) at 10 and 30 min and 'very significant' (p≤0.01) at 60 min; indicating that ash erupted from the Soufrière Hills volcano is more reactive and releases more iron, than the quarrying of aged deposits from the same source. Volcanic ash released more total iron than volcanic quarry dust, but this difference was not significant.

Table 5.5 Results of an unpaired 2-tail Welch's t-test conducted for EPR at 10, 30 and 60 min and for total iron released over days 1-9 on quarry dust and volcanic ash from the Soufrière Hills volcano.

Soufrière Hills Volcano Grouping Compared	Radical Production			Total Fe released
	10m	30m	60m	Days 1-9
Quarried volcanic deposits versus erupted ash	***	***	**	ns

5.4.3 Haemolysis in the <1mm and <10μm size fraction

David Damby (Durham University) ran sample MSC (cristobalite processed from sandstone) as a taught example, this is plotted by both particle concentration (see Figure 5.9a), and by particle surface area (Figure 5.9b). Several other samples (<1mm size fraction) were then run as a pilot study; they are shown in Figures 5.9c-d. The samples which elicited a strong haemolytic response (notably, PH01, PH02 and FT03) were re-run in an extended study along with a broader range of other samples representing mafic, intermediate and felsic quarry dusts and volcanic ash and greywacke as a non-volcanic quarry dust comparison (shown in Figure 5.10 a-d by particle concentration and Figure 5.11 a-d by surface area). As previous studies have shown that volcanic ash elicits a low haemolytic response (compared to DQ12), only one volcanic ash sample from each magma category was selected for comparison (Damby *et al.*, 2013, Horwell *et al.*, 2013). Red blood cells become fragile with age and their haemolytic potential increases concomitantly (Wilson *et al.*, 2000); therefore the controls (DQ12 and TiO_2) were run at the beginning, middle and end of the experimental period in order to give the most accurate mean, the effect of this however, is a large margin of error attributable to the results, shown on these graphs to 3σ. Tables with data showing haemolysis results across the full concentration tested are presented in Appendix III.

The percentage of haemolytic activity exhibited at varying concentrations is shown in Figure 5.9 c and d. A dose-dependent increase in haemolysis was observed with all the particle types tested. The % haemolysis exhibited by sample MSC is – in

Figure 5.9a (by particle concentration) – close to that of the positive control DQ12; in Figure 5.9b however, which has been adjusted for surface area, this sample is more haemolytic than the positive control. Haemolysis data are not typically shown by surface area (only by concentration, unless surface area can be taken into account at the measurement stage); however, these results highlight the importance of analysing the data both by concentration and by surface area, particularly when analysing particles with varying surface areas. The pilot study revealed that volcanic quarry dusts elicit a range of haemolytic responses, whilst the volcanic ash sample displayed very low haemolysis. There was also variation among samples from the same quarry (as observed in the mafic FT, intermediate PH and felsic TP) with the felsic samples giving the broadest range; one sample (TP04) of finished product from Te Puke was less haemolytic than the positive control, whilst another (TP05) of raw material was more haemolytic than the positive control.

The majority of quarried samples and all of the ash samples exhibited low haemolytic activity, often in the region of rutile, the TiO2 polymorph used as a negative (non-pathogenic) control. Samples from two quarries, however, were much more haemolytic, exceeding even the pathogenic DQ12 standard (quartz). One set of such samples were from Flat Top, New Zealand, which also exhibited significantly higher surface areas in comparison to the other samples. As it was not possible to normalise the particle quantities used in the haemolysis experiment by surface area this may be the controlling factor, although it is important to note that the Flat Top samples had a surface area of 8.33 and 10.81 m2/g (Chapter 4) which is very similar to the DQ12 surface area of 10.10 m2/g (Wilson *et al.*, 2000). The other set of samples is from Little Bay in Montserrat where the ancient Silver Hills volcanic complex was being quarried; their surface areas are 2.27 and 4.81 m2/g (Chapter 4) which are substantially lower than the DQ12 value. The results were therefore adjusted to express haemolysis by surface area (Figure 5.11) and subsequently both PH01 and PH02 were more haemolytic than DQ12 from the start of the reaction as shown in (Figure 5.11b), similarly, a concentration of 0.008 mg/ml for both FT01 and FT03 exceeded the haemolytic effect of DQ12 (Figure 5.11a).

Figure 5.9 Haemolytic activity of sandstone and a range of quarry dust and volcanic ash samples by concentration (a and c) and surface area (b and d) respectively. Results are average of n=3 with error shown to 3σ.

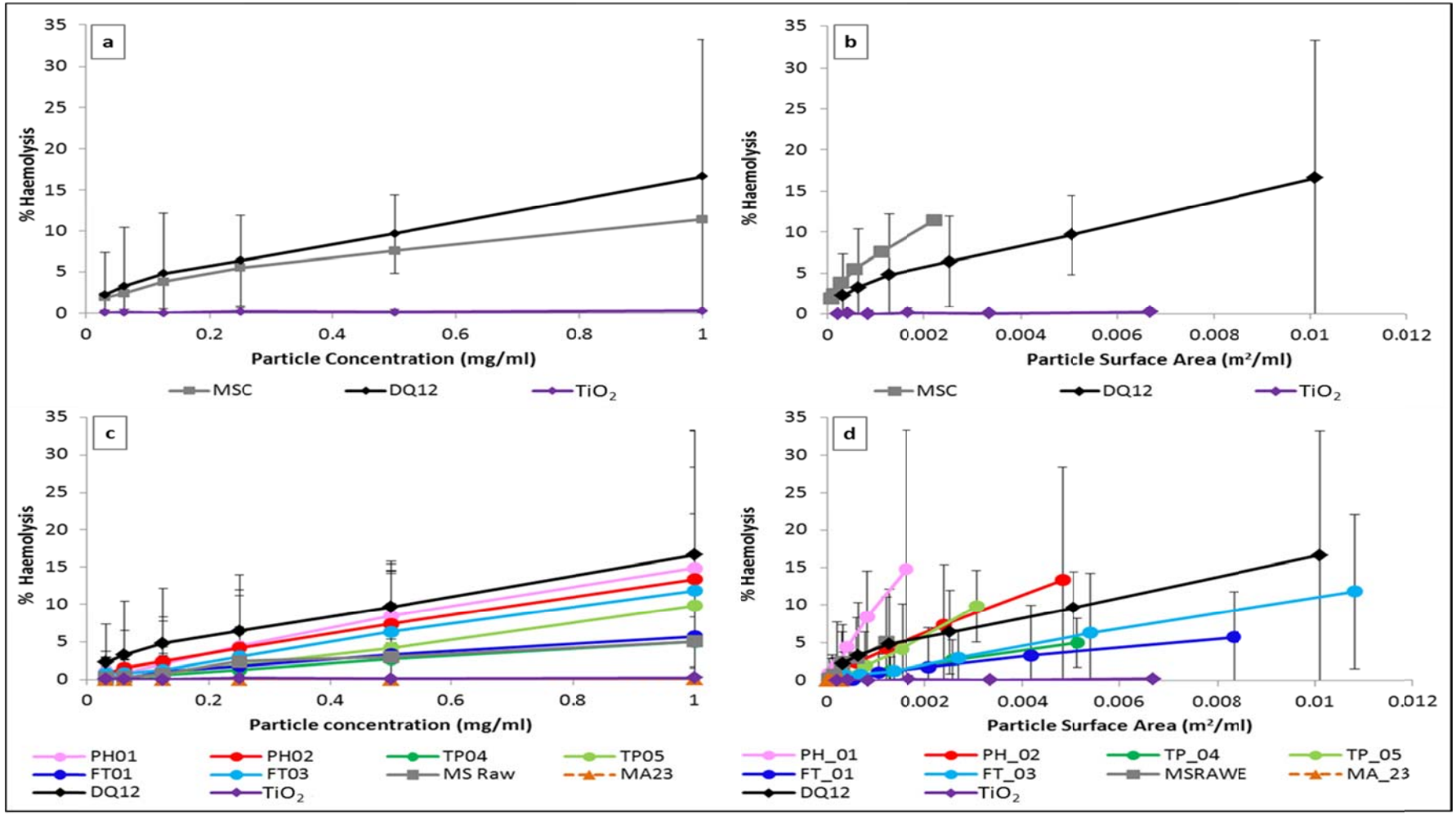


Figure 5.10 Haemolytic activity of volcanic quarry dusts and ash (a: mafic, b: intermediate, c: felsic) and greywacke quarry dust (d) by concentration. Results are average of n=3 with error shown to 3σ.

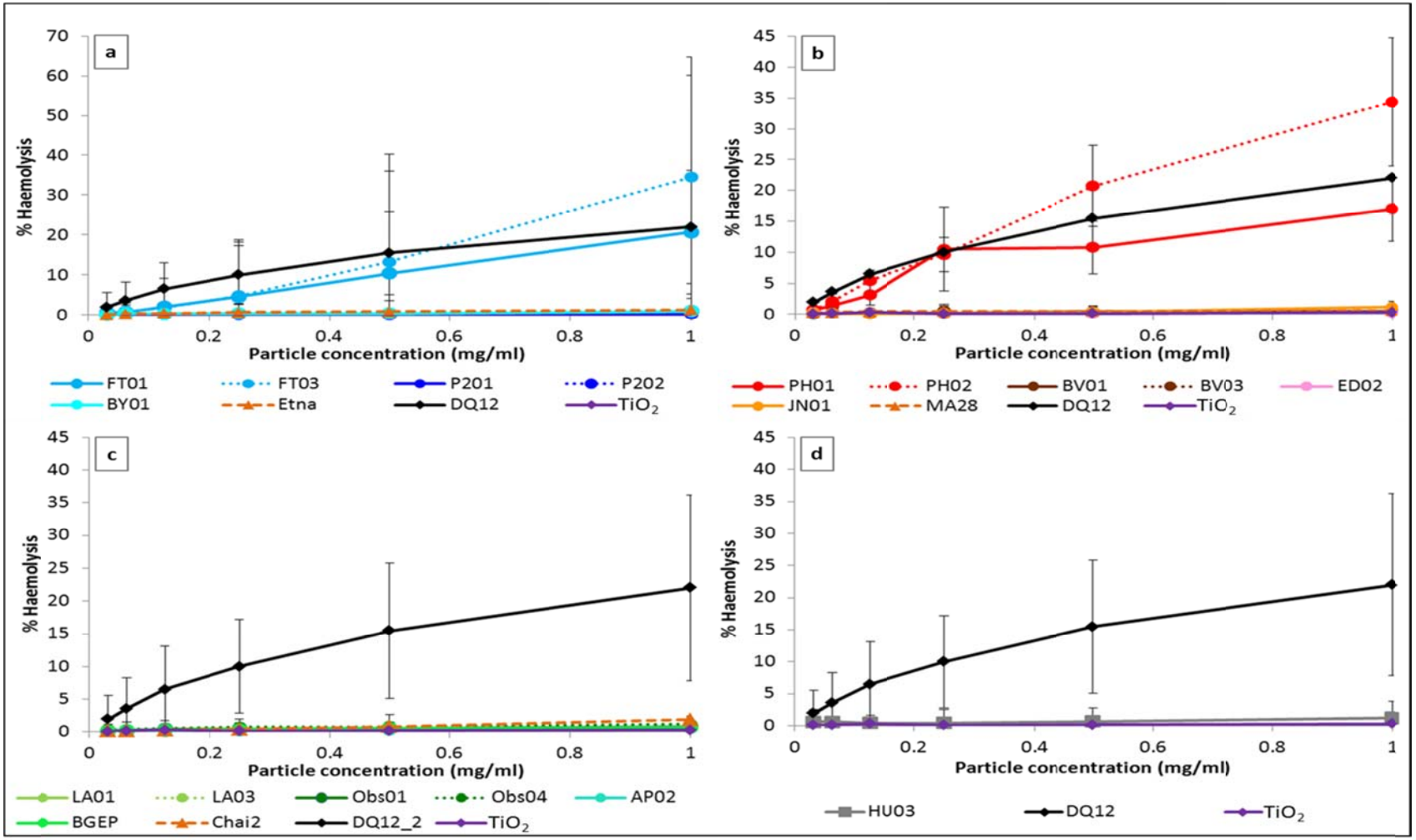
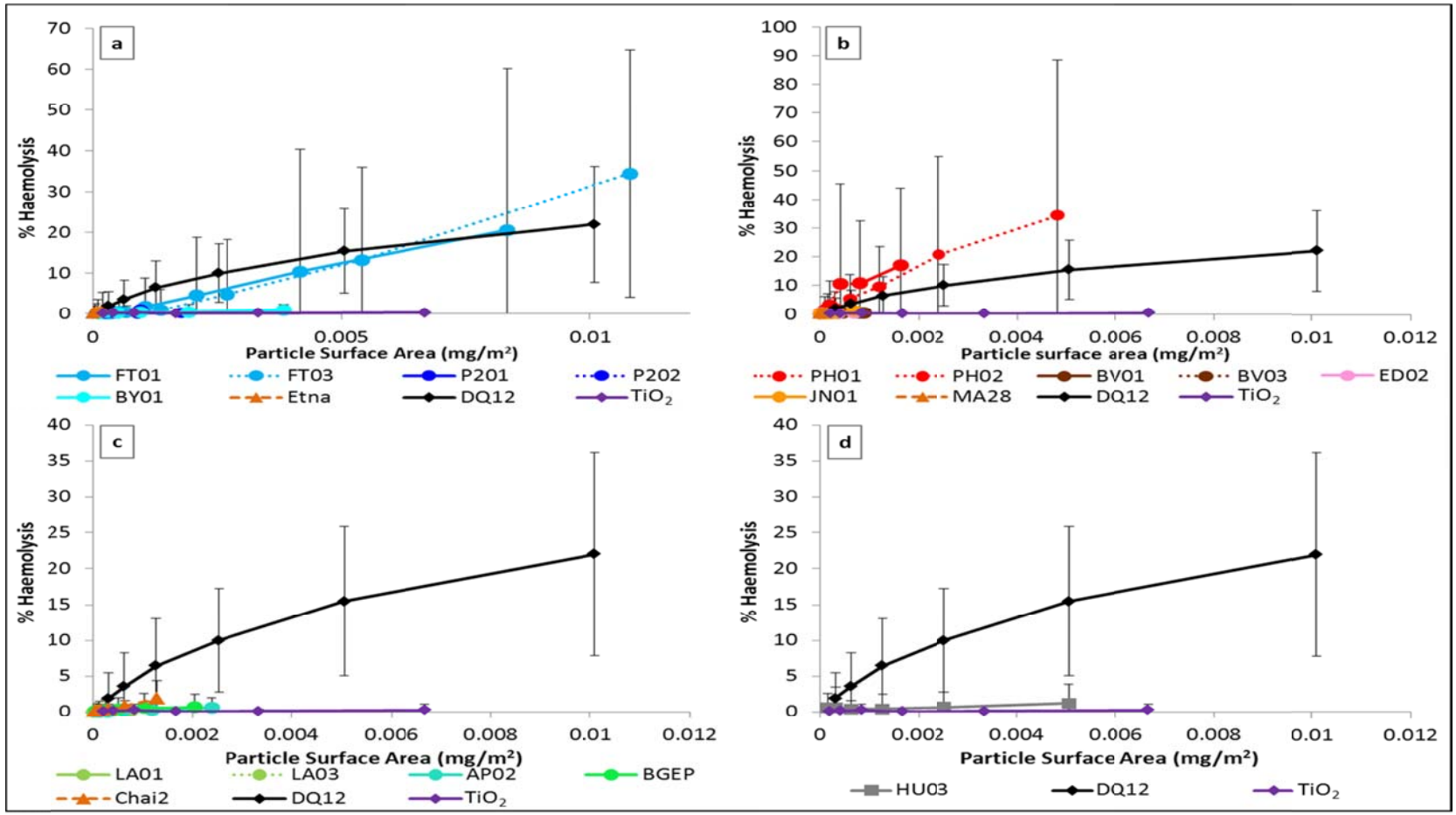


Figure 5.11 Haemolytic activity of volcanic quarry dusts and ash (a: mafic, b: intermediate, c: felsic) and greywacke quarry dust (d) by surface area. Results are average of n=3 with error shown to 3σ.



As several of the samples of volcanic quarry dust had elicited an elevated haemolytic response in comparison to the positive control, their size-separated PM10 (lung-pertinent) fraction was re-tested. These quarries were each from a different magma type: mafic Flat Top (FT), intermediate Phoenix (PH) and felsic Te Puke (TP) as well as the non-volcanic sandstone. In order to determine whether particle size was a potential driver of haemolysis, several non-haemolytic samples were also selected.

Due to the scarcity of sample it was not possible to run further surface area analyses on these samples and therefore they are presented only by particle concentration in Figure 5.12. The results obtained are similar to those in the earlier studies, with the samples from the volcanic quarries Flat Top, Phoenix, Te Puke (TP) and sandstone quarry Moneystone (MSR and MSC) eliciting a similar response to their counterparts in the <1mm fraction studies. Samples from Bombay (mafic), Henderson (felsic) and Hunua (greywacke) are all comparatively low, as they were in the <1mm analysis. This suggests that, for these samples, grain size was is unlikely to be a strongly contributing factor to their haemolytic potential.

These samples were also lightly re-ground so as to freshen their surfaces as this is known to increase haemolysis. Their grain size was tested before and after grinding to ensure that the grinding did not reduce their size (grain size results are presented in Appendix III). The results of the re-ground samples are presented in Figure 5.13. A one-tailed paired t-test was used to test for significance between the unground (Figure 5.12) and ground data with the hypothesis that grinding increases the haemolytic potential of the samples. Data were analysed using the statistical functions in Microsoft Excel and significance is indicated at *$p \leq 0.05$ and ** $p \leq 0.01$. The re-ground samples exhibited greater haemolysis, however, this increase was not statistically significant across all concentrations.

Figure 5.12 Haemolytic activity of sub-10 um volcanic quarry dusts and ash (a: mafic, b: intermediate, c: felsic) and non-volcanic quarry dust (d) by concentration. Results are average of n=3 with error shown to 3σ.

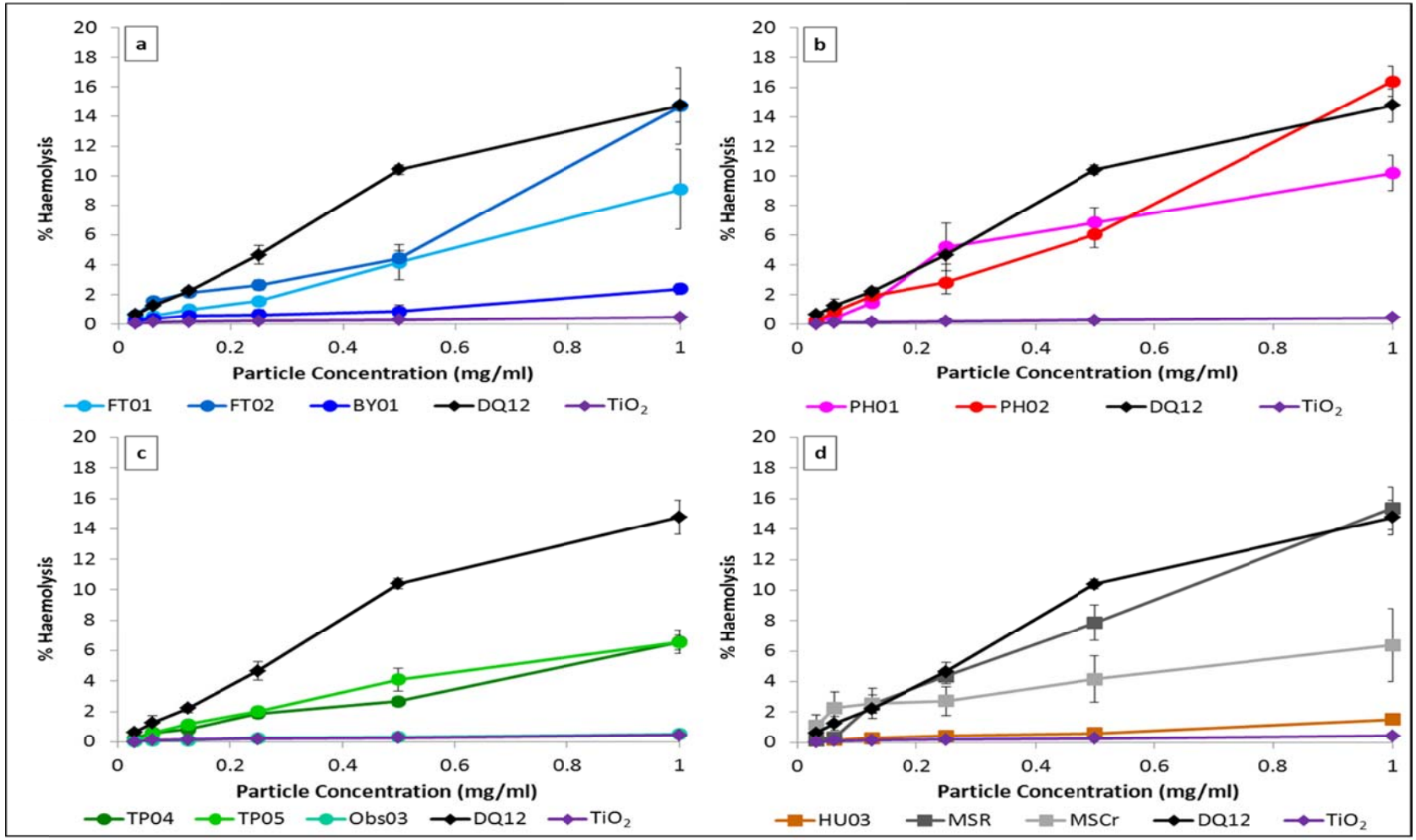
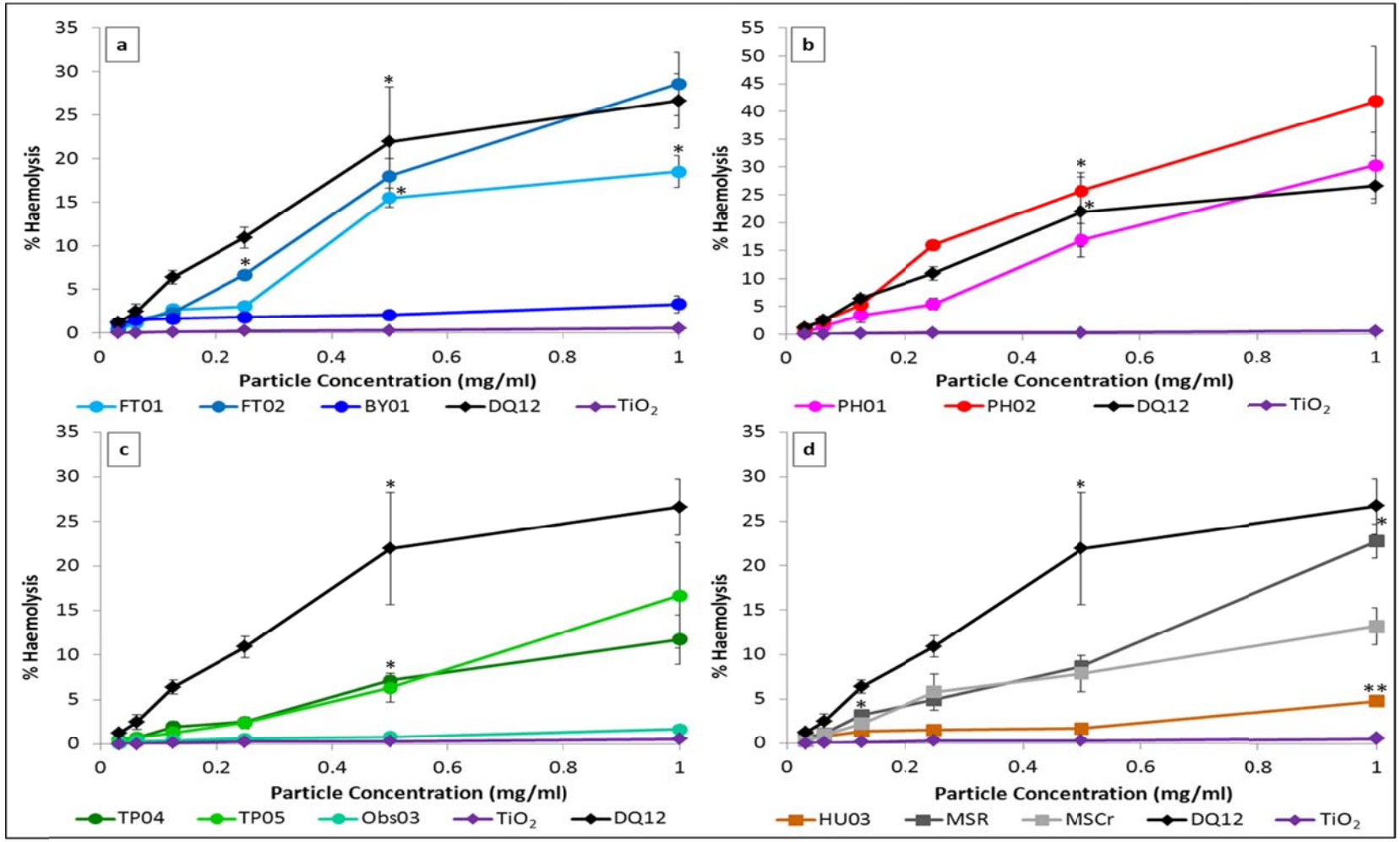


Figure 5.13 Haemolytic activity of re-ground sub-10 um volcanic quarry dusts and ash (a: mafic, b: intermediate, c: felsic) and re-ground non-volcanic quarry dust (d) by concentration. Results are average of n=3 with error shown to 3σ, statistical significance indicated as *P≤0.05 and **P≤0.01 (1-tailed paired t-test).

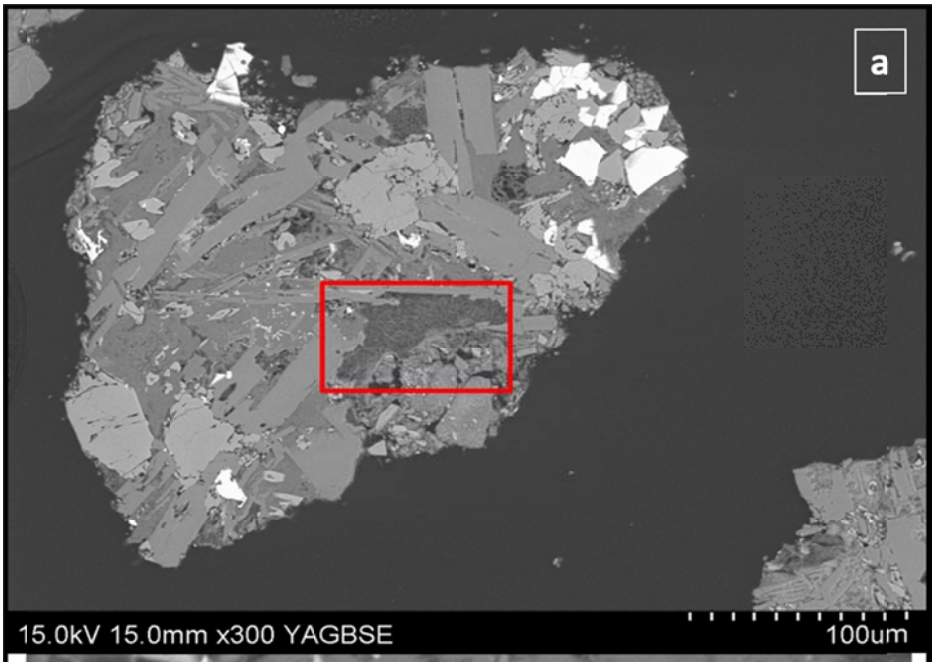


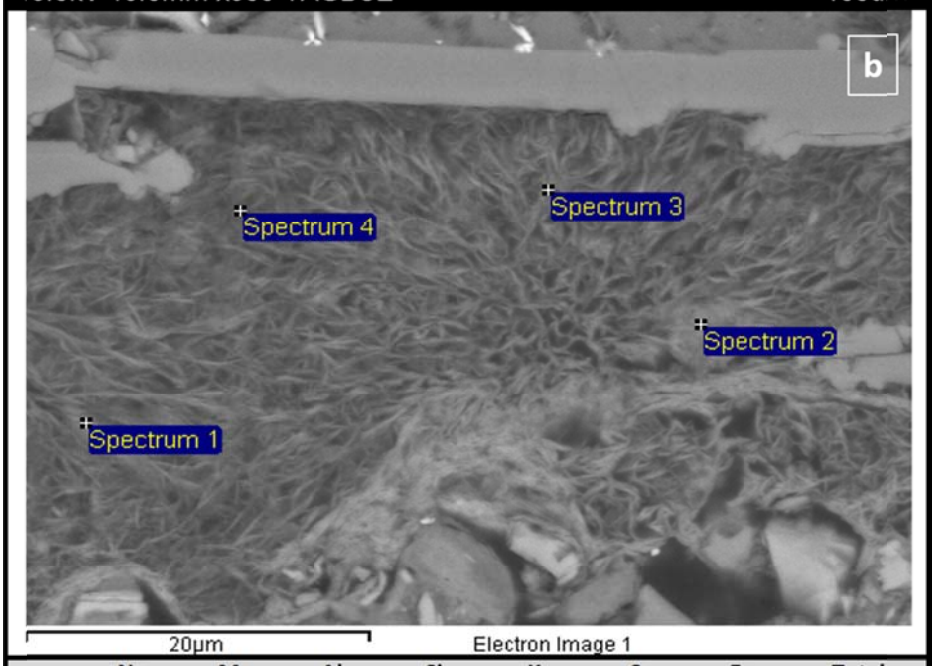
5.4.4 Clay Minerals

Four of the samples which elicited high haemolysis results (PH01 and PH02, FT01 and FT03) were made into resin blocks and minerals observed by SEM in polished cross-section. Clays were observed in samples from Little Bay, Montserrat (as shown in Chapter 4, Figures 4.25 and 4.26). A block from sample FT_03 shows an example of a particle which has areas where minerals are degrading into clays (Figure 5.14a). An elemental composition was taken of the feathery texture indicated in Figure 5.14a and this was interpreted to be clay (based on the parameters described in Chapter 4), as shown in Figure 5.14b.

As described in the methods (Section 5.3), for these samples, the clay fraction was also separated from the bulk and mounted onto slides for XRD analysis; there was a clear indication of clay present at the characteristic 5-7° 2θ area in PH01 and PH02 and the 32° 2θ area in FT01 and FT03; it was not possible to determine the exact clay type by comparing with standards. It is known, from the literature, that in the Flat Top deposit secondary phases include chlorite, smectite and illite clays (Nicholson *et al.*, 2000).

Figure 5.14 a) Clay texture observed in a dust particle from Flat Top quarry, New Zealand; b) magnification of area highlighted in image a); and the elemental compositions of the spectra 1,3 and 4, indicated in b) in elemental wt. %.





	Na	Mg	Al	Si	K	Ca	Fe	Total
Spec 1	0.76	8.73	11.25	47.44	1.51	1.78	28.54	100.00
Spec 2	0.56	6.03	11.33	55.70	3.57	0.86	21.95	100.00
Spec 3	0.79	8.75	11.90	46.97	1.12	1.88	28.60	100.00
Spec 4	-0.10	13.34	8.28	44.87	0.34	2.02	31.25	100.00

5.5 Discussion

5.5.1 Overview Summary

The overall aim of this chapter is to investigate the surface reactivity elicited by different quarry dusts and compare this with volcanic ash and non-volcanic quarry dusts. It is critical to investigate the differences amongst volcanic quarries worldwide, so that any controlling characteristics, which will vary among deposits, are recognised. For both the surface radical generation and iron release analyses, volcanic ash showed greater reactivity and greater variability than quarried material of comparable magmatic composition. This difference is likely to result from differences between quarry dust particle surfaces and erupted ash surfaces, as the former have long environmental residence times and will have experienced weathering. In the haemolysis assay, some quarry dust samples elicited a response comparable to that of the positive control; these were investigated further by testing a separated fraction of fine material and observing any differences as a result of grinding. Finally, an investigation into the presence of clays was conducted, which revealed that samples which had increased haemolytic potential contained minerals that had weathered to clays. Due to the potential presence of minerals altered by weathering, volcanic quarry dust ought to be considered a hazard distinct from volcanic ash, particularly for mafic and intermediate compositions; rhyolitic eruptions are comparatively rare and require further investigation with a larger sample set.

5.5.2 Appraisal of hypotheses and wider implications

1) *Dust from quarried mafic material exhibits greater surface reactivity, than dust from intermediate or felsic quarries.*

Mafic magmas contain more iron-bearing minerals compared to more siliceous magmas; however, the iron-bearing minerals must occur on the particle's surface in order to potentially participate in the Fenton reaction. No significant difference was found in the generation of hydroxyl radicals by mafic quarry dust samples in comparison to intermediate or felsic quarry dust; however, mafic quarry dust samples released significantly more iron than their intermediate or felsic counterparts.

A one-way ANOVA with Bonferroni correction revealed no significant difference was between the radical generation of mafic and intermediate or mafic and felsic dusts; however, intermediate dusts released significantly more radicals than felsic dusts at 30m and 60m. This suggests that due to the poor Fe-content of felsic magmas their propensity to generate radicals is very limited. For iron release, there was no significant difference between intermediate and felsic dusts; however, mafic dusts released significantly more iron than both intermediate and felsic dusts, this may be due to the increased contents of bulk iron (mafic magmas are richer in iron) resulting in commensurate iron availability on particles surfaces. This is supported by the fact that the total iron released by mafic quarry dust was significantly greater in comparison to the intermediate and felsic dusts; in volcanic ash samples hornblende and pyroxene were found to be the source of radical production in volcanic ash samples (Horwell *et al.*, 2007). It is possible however, for poorly co-ordinated iron to be available on particle surfaces but not to instigate radical production (Horwell *et al.*, 2003a), which indicates that the relationship between Fe-content and Fe-release and also radical generation is not straightforward, as demonstrated by a lack of clear correlation between radical generation and iron release. The reasons for this are discussed in more detail for hypothesis 2.

The range exhibited by mafic and intermediate quarry dusts was not extensive enough to be statistically significant between these two groupings; but it is not possible to say whether a larger set of quarried samples (with a greater range of

exhibited reactivity) would yield a statistically significant difference. Conversely, there was no significant difference between the amount of total iron released by intermediate and felsic samples; whilst there was a concurrent significant difference in radical production at 30 and 60m. The intermediate samples originated from eruptions of the Silver Hills and the Soufrière Hills volcano Montserrat and ash from the latter is known to generate radicals from the iron contained in ferromagnesian silicates such as amphibole (Horwell et al, 2003).

2) *Drilling/blasting mafic lava produces dust which is more reactive than fragmentation of magma during mafic volcanic eruptions.*

Drilling and blasting of mafic lava in quarries may produce dust which is finer-grained and with a higher surface area than magmatically-equivalent volcanic ash samples (as demonstrated in Chapter 4) because mafic eruptions tend to be effusive, generating rather coarse ash; the mechanical fragmentation in quarries may create different surface functionalities compared to erupted tephras, resulting in different surface reactivity between quarried and erupted particulate, as well as different grain size and surface area. Mafic volcanic ash produced significantly more hydroxyl radicals and released significantly more iron than mafic quarry dust (as shown in Table 5.4). Freshly generated mafic quarry dust, therefore, is less reactive than erupted volcanic ash and should be considered as distinct in terms of potential hazard, making ash a poor analogue in this case. As the mafic quarry dust did, however, release appreciable quantities of hydroxyl radicals (up to 0.36 µmol/m^2), it may potentially pose a hazard in certain quarry settings, for example drilling and blasting where the quantity of PM10 is highest (as shown in Chapter 4). These results can be used to inform hazard based on potential reactivity but ought to be considered in tandem with the exposure of workers in order to fully appraise the hazard posed.

Whilst this hypothesis must be rejected, it is important to consider why the freshly cleaved surfaces of fine-grained drilled mafic quarry dust were so much less reactive than erupted mafic ash, which is often comparatively coarser-grained (as shown in Chapter 4, Figure 4.9a). Volcanic ash passes through a plume during eruption and this provides an opportunity for volatiles to deposit on ash particle surfaces; including sulphur, halogen and metal species (Witham et al., 2005). Many volatile metal elements are released during a volcanic eruption (Allard et al., 2000), which can

deposit on ash surfaces and can subsequently be removed by weathering which leads to their dispersion in the environment (Witham et al., 2005). A review into leaching of such metal elements and other volatiles by Witham et al. (2005) reveals that there are many factors which control the adsorption of volatile elements onto ash particle surfaces including: the composition of the magma and tephra, mode of eruption, gas-pyroclast dispersion following fragmentation; concentration of the plume; ratio of particles to gas; particle size-fractions and surface area, porosity and texture, temperature and chemical history of the particle trajectory through the plume, environmental conditions (e.g. wind, humidity), and the extent of hydrothermal interaction within the volcano. These processes may account for the wide-ranging variability in the reactivity exhibited by mafic ash particles. All of the ash samples analysed here were specifically selected on the basis that they were collected fresh before weathering could occur (they were stored in air-tight containers). Conversely the samples from quarries have existed in the environment for long periods of time and have been subjected to weathering which may affect the reactive iron on their surfaces, for example, hydrothermal alteration may lead to non-magmatic Fe-bearing phases e.g. clay, sulphides (Ayris & Delmelle, 2012), however this Fe may not necessarily be reactive as not all iron on the surface is available for free radical release, e.g. iron on particle surfaces in the form of Fe_2O_3 and Fe_3O_4 is inactive (Fubini *et al.*, 1995b) and an excess of iron can also lead to a reduction in reactivity (Elias *et al.*, 2002, Gulumian, 2005). This environmental residence time may account for the lowered reactivity exhibited by mafic quarry dust compared to mafic ash.

Finally, the oxidation state of Fe itself, can change following inhalation as the lung lining can both chelate (due to metal-binding proteins) and reduce (interaction with ascorbate or superoxide ions) (Damby, 2012, Fubini & Otero-Areán, 1999). The relationship between iron on particle surfaces and resultant reactivity is, therefore, complex.

3) *Intermediate and felsic quarry dusts will generate more haemolysis that mafic quarry dusts.*

In the haemolysis assay, several quarry dust samples exhibited elevated haemolysis from each of the magmatic groupings, whilst others caused a negligible response. The mafic samples from Flat Top, intermediate samples from the Silver Hills Complex, and

the felsic samples from Te Puke all exhibited a haemolytic response comparable to the DQ12 positive control. The crystalline silica content of the intermediate samples was substantial at 18-19wt% but the content of the felsic samples was only 3-6wt% and that of the mafic samples was below the limit of detection. Therefore the cause of haemolytic activity here cannot be the presence of either quartz or cristobalite.

The factor which these haemolytic samples have in common is that they contained clays. Over long periods of time, certain volcanic minerals, particularly feldspar, can weather to clays, as has been observed in a range of magma types (Aomine & Wada, 1962, Eggleton *et al.*, 1987). Certain clays can actually cause haemolysis themselves, particularly kaolin (Love *et al.*, 1999, Wallace *et al.*, 1988) and smectites (Oscarson *et al.*, 1986, Williams & Haydel, 2010, Williams *et al.*, 2009) which are being trialled as antibacterial agents due to their ability to cause cell lysis (Williams & Haydel, 2010, Williams *et al.*, 2009). It is appropriate for haemolytic samples to be investigated further; however, a positive result does not necessarily indicate toxicity as haemolysis is not indicative of a positive disease endpoint.

Four of the samples which elicited high haemolysis results (PH01 and PH02, FT01 and FT03) were investigated for the presence of clays. The XRD patterns of the separated clay fraction, appear characteristic in the 5-7° 2θ area for PH01 and PH02 and the 32° 2θ area for FT01 and FT03 (Velde, 1992); however, matching against standards to determine a specific clay mineral was not possible. It is known from the literature, thatthe Flat Top deposit secondary phases include chlorite, smectite and illite clays (Nicholson *et al.*, 2000). Analysis of dust in resin blocks showing particles in cross section, reveal areas of weathering and feathery textures interpreted as clay by SEM-EDS. The presence of clays is likely to be the causative agent in the haemolytic response observed here, particularly as the FT samples contained very little crystalline silica and, although the PH samples contained an appreciable amount, crystalline silica of volcanic origin has not previously produced a haemolytic response. The signal from crystalline silica (as opposed to clays) can be tested by incubation with aluminium lactate which has been shown to dampen the signal from quartz (Duffin *et al.*, 2001) and is discussed as part of further work in Chapter 8.

4) *The extraction and processing of material produces dust with fresh surfaces which is more reactive than the dust accumulated on the quarry floor or the stockpile.*

It is likely that in a quarry, material which has been mechanically fragmented through crushing or abraded through screening, might have fresher surfaces than material lying on the quarry floor or in stockpiles. The results of this study are inconclusive with regard to differences in reactivity between dusts variously extracted and processed.

From Tables 5.2 and 5.3, it is possible to compare final product dust samples (collected from stockpiles) with raw, drilled and processed samples at Flat Top, NZ (FT01 and FT03), Belham Valley, Montserrat (BV01 and BV03), Te Puke, NZ (TP04 and TP05) and Yali, Greece (AP02 and LA02). In each case, the final product sample has a higher surface area than the other samples which may result from surface abrasion during processing. Additionally, each final product sample contained slightly less removable Fe^{2+} than their counterparts, perhaps as a result of oxidation by weathering or wetting during processing. However, in terms of reactivity, the $HO^{\cdot}$ generation data were so low and in such a narrow range (0.03-0.79 μmol/m^2) that it is not possible to make any inferences as to whether the slightly reduced Fe2+ content impacted on the radical generating potential.

Samples from Flat Top and Little Bay (<1mm fraction), show the greatest haemolytic response , which include one sample each of drilled or processed dust (FT01 and PH01 respectively) and one sample each of dust from finished product (FT03 and PH02). In order to determine whether fresh grinding has a significant impact upon particle surfaces in haemolysis, a follow-up was conducted on the size-separated PM10 fraction. Samples which had indicated haemolytic potential were selected: mafic Flat Top (FT), intermediate Phoenix (PH) and felsic Te Puke (TP) as well as the non-volcanic sandstone, and in order to determine whether particle size was a potential driver of haemolysis, several non-haemolytic samples were also selected: Bombay (mafic), obsidian (felsic) and Hunua (greywacke) as a non-volcanic comparison. There was increased haemolysis exhibited at a few of the concentrations of a few of the samples as shown in Figure 5.13 as determined by a 1-tailed paired t-test; however, there was no systematic significance detected. For the haemolytic volcanic quarry samples this is

likely to be due to the fact that their haemolysis resulted from secondary phase clay minerals and so refreshing the surfaces of clays makes no appreciable difference to the haemolytic activity. Any freshly cleaved crystalline silica, such as in the intermediate Phoenix samples, appears to be no more haemolytic than in the un-reground quarry dust.

Confirmation of differences between freshly-processed dusts and dusts which had longer residence time in the quarry, would allow occupational health advice to be devised for specific roles where workers were exposed to more hazardous particulate (e.g. workers frequently drilling/clearing blasted material or conducting processor maintenance); however, it is likely that a much larger sample set would be required for conclusive results within each magmatic grouping. One factor that should be considered, however, is whether the processing is wet or dry, as wet processing is likely to reduce dust levels, as well as, affecting surface freshness. Many quarries undertake dry screening initially, to manufacture their smallest size of finished product (hence the dust samples from finished product collected here were selected from the smallest grade of finished product manufactured) and then the material which was separated as too large, is further wet-screened to remove any remaining fines and separated into larger sizes of finished product.

This hypothesis cannot be accepted on the basis of the limited data here, however, broader analysis on a greater range of samples may elucidate some of the confounding factors expressed here.

5) *Quarrying friable, intermediate deposits from pyroclastic density currents or lahars produces dust which is less reactive than erupted ash from the same source volcano.*

Samples of volcanic ash from the Soufrière Hills volcano used in this study were collected fresh upon deposition whilst quarried Soufrière Hills volcano samples were collected from pyroclastic density current (PDC) deposits at Trants and lahar deposits in the Belham Valley. The quarried deposits are likely to have been exposed to percolating vapours, meteoric water and channelled water flow, resulting in weathering and reduction of their surface reactivity (due to iron oxidation). The Soufrière Hills volcanic ash did generate significantly more radicals than quarry dust

from Soufrière Hills volcanic deposits, but the difference in iron release was not significant, however the ratio of Fe2+ to Fe3+ may be a contributing factor.

Significance in the differences observed was determined through an unpaired 2-tailed Welch's t-test, shown in Table 5.5, which revealed that the difference in radical production was 'extremely significant' ($p \leq 0.001$) at 10 and 30mins and 'very significant' ($p \leq 0.01$) at 60 mins. Whilst volcanic ash released more total iron than volcanic quarry dust, this difference was not statistically significant.

The significant increase in radical production may be due to grain size and crystalline silica content. Horwell et al., (Horwell *et al.*, 2001, Horwell *et al.*, 2003b) showed that PDC and lahar deposits are coarser, and contain less crystalline silica than co-PDC ashfall deposits, due to fractionation of the smaller, less-dense particles by elutriation into the lofting co-PDC plume (in the case of PDCs) or lahar flow, leaving a fines-depleted deposit. It is probable that erupted ash is more reactive than quarry dust because it will have retained the freshly fractured surfaces, it is fines-enriched, and is not exposed to moisture other than within the volcanic plume, where it is likely to have a variety of elements adsorbed onto its surface.

This hypothesis is therefore correct on the basis of the samples studied here. It also indicates that volcanic ash can be a poor analogue for the reactivity of quarry dust, even when it is taken from the same magmatic source.

5.5.3 Comparison of dust from volcanic quarries with non-volcanic quarries

The non-volcanic quarry samples varied in their reactivity with the MSR sandstone sample generating radicals comparable to intermediate ash samples; whilst the HU greywacke sample generated very few, but more than the Min-U-Sil quartz standard. Both samples released less iron than mafic quarried and erupted ash samples, but the raw sandstone MSR and sandstone processed into cristobalite MSC elicited haemolysis similar to that exhibited by the positive control. The greywacke sample contains far less crystalline silica than the sandstone sample (up to 98 wt.%) and this is commensurate with its haemolytic response. This is significant because much focus has been given to rocks such as sandstone and greywacke which are highlighted by organisations such as IARC (1997) as being of concern due to their crystalline silica

content, however, here the greywacke has been shown to be of a comparable hazard to volcanic quarry dusts in terms of surface reactivity and potential toxicity, whereas the sandstone was comparable to volcanic ash in terms of radical production, but potentially more toxic in terms of haemolysis. This discrepancy highlights the problematic nature of silicosis and the limitations of knowledge regarding the mechanism by which quartz causes disease, the amount of other minerals present in addition to crystalline silica by dampening the haemolysis seen here. A study by Clouter et al. (2001) analysed workplace sandstone samples by haemolysis and compared them to the DQ12 standard. Clouter's samples of sandstone are similar (in terms of crystalline silica purity) to the Moneystone sandstone sample studied here. Both Clouter et al. and this study found that DQ12 is more haemolytic than the sandstone samples.

There has been some work on the reactivity of other quarried dusts, such as the investigation by Øvrevik et al (2006) on mylonite, gabbro, basalt, feldspar, jasper and quartz from Norwegian quarries. They investigated the correlation between iron release and hydroxyl radical generation from mineral particles, the death of human alveolar epithelial cells and the release of the cell protein cytokine (indicating a pro-inflammatory response) (Øvrevik *et al.*, 2006). This study found that soluble iron did not correlate with radical generation and that neither of these parameters were required for either the inflammatory potential or the cytotoxicity of many mineral particles. The study did find, however, that basaltic dust induced cytokine release more strongly than feldspar, gabbro or quartz dusts, despite the basalt and gabbro containing similar quantities of iron (Øvrevik *et al.*, 2006). Øvrevik et al's iron release and hydroxyl radical generation data are broadly comparable to those in this study, despite using different amounts of reagent and sample in their methods; however, due to these differences in study design, it is hard to extrapolate the results of their *in vitro* studies to the potential toxicity of the samples used here. In addition, they sourced their samples from university archives rather than collecting them fresh from the quarry face so storage conditions may also have affected their analytical findings.

5.5.4 Comparison of <1mm fraction with ≤10µm fraction and previous work by others.

The haemolysis of the samples of the <1mm fraction and the <10µm separated fraction are presented in Table 5.6 whilst those conducted in the same laboratory by David Damby are presented in Table 5.7.

Table 5.6 The haemolysis in % at 1mg/ml for <1mm fraction and <10µm fraction for a variety of quarry dusts.

Sample	<1mm bulk	≤10µm separated
FT01	5.72	3.41
FT02		4.06
FT03	5.84	
BY01	1.38	3.04
PH01	14.86	16.35
PH02	13.37	5.91
TP04	5.00	4.72
TP05	9.84	4.70
HU03	1.21	1.41
MSR	5.05	11.38
MSCr	11.39	12.01
DQ12 for <1mm	16.63	
DQ12 for ≤10µm	18.03	
TiO_2 for <1mm	0.24	
TiO_2 for ≤10µm	0.51	

Table 5.7 The haemolysis in % at 1mg/ml for <1mm fraction and <10µm fraction for a variety of volcanic ash samples (Damby, 2012).

Sample	<1mm bulk	≤10µm separated
Colima	0.08	2.51
Merapi	0.35	1.02
Merapi Pyroclastic flow	0.42	0.24
Mt St Helens	0.39	0.38
Soufriere Hills	0.2	0.61
Unzen	0.09	0.13

For the samples in this study (Table 5.6) there is very little difference in the haemolysis between the <1mm fraction and the separated fraction. As the analyses were run at different times, natural variability (both in samples and in red blood cells) as demonstrated by the standards precludes statistical comparison. It can be seen, however, that overall the sample grain size does not greatly influence the sample's haemolysis even for those samples which had comparatively high haemolysis (e.g. PH01 which gave 14.6% in the bulk <1mm and 16.35% in the separated fraction). Some samples gave a slightly higher reading for the separated fraction (compared to the <1mm bulk) whilst others gave a lower one, but this is likely to be in keeping with natural variation.

A similar relationship can be seen in the samples studied by Damby (2012), where Colima and Merapi gave slightly elevated haemolysis in the separated fraction (up to 2%); however as overall haemolysis for these samples was low this is also likely to result from natural variation between subsamples. Finally, similar analyses on diatomaceous earth has also revealed no significant difference (statistically tested) between the separated and <1mm fractions (Nattrass, In prep.).

These results therefore indicate that particle size is unlikely to be the main driver of haemolysis, it is far more likely that the surface area of particles will play a bigger role in haemolysis and this is explored in more detail in Chapter 8.

5.6 Conclusions

The limited range of surface reactivity and toxicity experiments undertaken here give a first indication that volcanic quarry dusts are less reactive than erupted ash from comparable magma types, even when samples contain similar quantities of crystalline silica and respirable material and have similar bulk chemical compositions. This has been clearly demonstrated for both mafic and intermediate magma types. The quarried felsic samples studied here have demonstrated low reactivity comparable to that of an ash sample of felsic origin; however, analysis on a larger sample suite

(particularly for volcanic ash, as rhyolitic eruptions are comparatively rare) may produce more conclusive results. This comparative increase in reactivity of ash is likely the result of ash particles not being weathered and also potentially because they have modified surfaces resulting from plume interaction.

Quarry dust reactivity does not follow the same trend as is broadly observed for volcanic ash (the association of higher iron release with a greater quantity of radical generation). There are subtle differences, in the nature of the hazard posed by mafic and intermediate magmas, however, with mafic dusts releasing more iron and the intermediate dusts potentially able to generate more radicals. This has implications for hazard management because it highlights that some quarry settings warrant further investigation and highlights the need to define volcanic hazards more specifically. The observed lack of clear association between iron release and radical generation, also supported by Øvrevik et al's study (Øvrevik *et al.*, 2006), indicates that for quarry dust the measured iron release is not always a useful indicator of likely radical production.

The inference that quarry dust could potentially be less toxic than erupted ash should not be used for hazard assessment purposes as this study only investigated two assays related to particle toxicity and there are many other mechanisms that might be involved in particle pathogenicity in the lung. In addition, the levels of occupational exposure are critical. Volcanic activity may occur on the order of days to decades (such as on Montserrat) and exposure to ash occurs due to ash fall events, post-event clean up and re-suspension (which can last months to years). The exposure to individual volcanic events may be greater than in an occupational setting (to be determined in Chapter 6) but the duration of exposure is incomparable. Many workers spend their entire working lives in quarries exposed to particulate on a daily basis for decades, which means that a longer-term exposure to a comparatively less toxic dust may be, potentially, more harmful. This can only be determined by measuring the exposure levels and assessing the dust mitigation strategies which workers employ. This is explored in the next chapter.

This chapter has indicated that volcanic dusts can exhibit toxicities which are comparable (in certain experiments) to those of non-volcanic origin. It may be worthwhile considering, therefore, whether volcanic quarry dust ought to be given

equal consideration (regarding potential respiratory health impacts) as is afforded to silica-rich rock. This is particularly important in light of the fact that toxicity mechanisms for silica-induced pathogenesis are unclear and rocks are composed of varying and sometimes complex mineralogies.

In the samples investigated here, processing increases the surface area of particles, but when this parameter is accounted for, processing has little or no impact upon reactivity. This has direct implications for attempts to determine hazard level on the basis of a worker's specific role, i.e. extraction cannot be considered more hazardous than stockpiling or vice-versa. Whilst the potential toxicity indicated, and the reactivity of the dust itself, may not vary by quarry role, the exposure to such dusts can; therefore, the following chapter aims to determine whether there are appreciable differences in the levels of dust exposure among different roles and among the same activities at different quarries, thereby completing a holistic assessment of the potential airborne hazard of quarrying volcanic deposits.

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Chapter 6 – The Exposure Hazard of Volcanic Quarry Dust and Associated Risk Management

6.1 Introduction

The previous chapters have investigated the physical, chemical and toxicological characteristics of quarry dusts; whether those dusts identified as potentially hazardous do, in fact, pose a risk is influenced by the level of dust exposure. Exposure levels are determined by two principal factors: i) the concentration of dust in the air and ii) the amount of this dust inhaled. The first factor can be mediated through quarry-wide mitigation measures, whereas, the second factor is affected by any personal protective equipment workers use.

This chapter explores the issue of occupational health in quarrying, with a focus on exposure (legislation and means to mitigate) and describes the dust management strategies observed. The airborne dust concentrations in the quarries was measured both as background levels (in different parts of the quarry) and as personal exposures (for different roles within the quarry). Dust management was assessed through an ethnographic study and a pilot-scale, questionnaire-based survey; the latter yielded qualitative information (presented in Appendix IV) which could be used to inform the design of a larger-scale study.

6.1.1 Quantifying the Occupational Risks of Quarrying

Mining and quarrying have the highest occupational death rates in many countries around the world. In the U.S.A., during 1980-1995, the rate was 30.3 in every 100,000 (from all causes); the next most dangerous occupation was agriculture with a rate of 20.1 deaths in every 100,000 for the same period (Center for Disease Control, 2012). Age-adjusted mortality rates for silicosis in the U.S.A. were 0.7 per million in 2004 (Leung *et al.*, 2012). In the U.K., the Office for National Statistics has investigated occupational mortality in England and Wales (for the period 1991–2000) and the data are dominated by occupation-specific causes of death which relate to respiratory morbidity, including: cancer, chronic obstructive pulmonary disease, silicosis, pneumoconiosis and asbestosis (Coggon *et al.*, 2009). Miners (excluding coal) and quarry workers in England and Wales, showed statistically significant, raised death rates due to silicosis, tuberculosis and other

pneumoconioses (Coggon *et al.*, 2009, Coggon *et al.*, 2010). In New Zealand, during the period 2000-2005 the highest overall death rate (by occupation) was for plant and

machine operators and assemblers, even after standardising the data for socio-economic deprivation (Holmes *et al.*, 2011). Age-standardised (15-64 years old) mortality rates (number of deaths per 100,000 person-years at risk) revealed a figure of 14.7 for respiratory diseases (higher than for any other occupational grouping) and 132.1 for cancer (Holmes *et al.*, 2011).

6.1.2 Controlling Exposure to Dust in Quarrying

Dust in quarries is created by tearing, breaking, blasting, sawing, drilling, crushing, grinding, sanding, filing, or otherwise abrading a material (Cotes & Steele, 1987). A variety of methods exist to reduce levels of respirable dust, which include best practice methods of quarrying (suppression, collection, containment (Health and Safety Executive, 2008)), education and inspection (Cotes & Steele, 1987)). A detailed list of these principles is presented in Table 6.1 and many have become best practices endorsed by regulatory bodies such as the UK Health and Safety Executive (HSE; (Health and Safety Executive, 2008). The MinEx Health & Safety Council of New Zealand has published similar guidelines for minimising workplace exposures during different processes (MinEx Health and Safety Council, 2008). EU-wide legislation for urban air pollution, including PM10 (particulate matter <10 μm), raised concerns regarding the breaching of permissible levels in parts of London and led to a recent experimental study that used the targeted application of calcium magnesium acetate to roads to bind the dust particles to the road surface. Early indications suggest that the air quality was improved (Deakin & Ren, 2011) and so a variant of this method might be applicable also to quarries.

Table 6.1 Principles of supressing dusts in quarrying. After Cotes and Steel (1987).

Principle	Detail	Example
Substitution	For safer material	Use substitute abrasive (not sand) in blasting operations
	For safer process	Use non-asbestos insulators
Dust suppression	Less dust produced	Use non-abrasive processes
	Less dust airborne	Reduce energy transfer
	Dust removed	Apply water to source: filtration, precipitation, centrifugation, scrubbing
Enclosure	Of the plant	Automated processes
	Of individual machines	
Segregation	With respect to time	Maintenance and repairs
Exhaust ventilation	Of enclosed process	Maintenance and repairs
	At single site via cowl	Machine or process liberating dust
	Mobile with hose	For use in confined spaces
General ventilation	Increased turnover of air	Any dusty process
Respiratory protective equipment (RPE)	Respirator or mask	Servicing dusty equipment
	Breathing apparatus	Fire in confined space
Good Housekeeping	Tidying, sweeping, vacuuming, washing	All places where work is done
Education	Recognized courses	Apprentices
	Pre-Employment	All personnel
	Periodic	All personnel
Inspection	Safety Officer	Daily or weekly
	Inspectorate	When problems suspected

Water is commonly used to dampen dust and prevent it from becoming suspended or re-suspended, both as part of processing and on larger areas (e.g. roads). Figure 6.1 shows water being used in a processing plant at Hunua quarry in New Zealand.

Figure 6.1 Water sprays over the processor at Hanua quarry, New Zealand, inset: magnification of sprays featured in central portion of the main photograph.

In terms of reducing occupational exposure, respiratory protective equipment (RPE) is considered to be secondary to minimising the dust levels at source (Graveling *et al.*, 2011). A review of published and unpublished literature and consultancy reports conducted by Graveling et al. (2011) explored the factors that influence a worker's decision with regard to whether they wear respiratory protection. The influences were found to be complex and variable, but the key factors included:

- Discomfort (including: resistance to breathing, pressure, chaffing, thermal discomfort, impaired communication/other activities).
- Lack of time
- Perception of low risk
- Disbelief in efficacy
- Management attitudes (e.g. example set by managers)
- Frequency of required use
- Type of mask
- Individual experience (e.g. health symptoms).

Graveling et al. (2011) made several recommendations in order to change perceptions and increase the use of RPE:

- Managers (at all levels) need to appreciate the requirement of RPE.
- Employees need to realise their role in an effective risk reduction programme.
- Managers should provide technically-appropriate (hazard-specific) RPE compatible with other personal protective equipment which fits the worker.
- Managers should provide information to workers regarding hazards and also proper training (including how to correctly fit and use a dust mask).
- Managers need to make provision for cleaning, maintenance and storage of dust masks.

6.1.3 Guidelines and Legislation to Limit Workplace Exposure to Quarry Dust

Workplace exposure limits vary from country to country – although permissible levels are often similar amongst those countries which use statutory regulation – and are generally referred to as workplace exposure limits (WEL, New Zealand) and occupational exposure limits (OEL, Europe and Canada). They are usually based upon an 8-hour time weighted average (TWA) which represents the duration of a typical daily shift.

The New Zealand government WELs (8 hr TWA) give permissible levels for dusts which contain <1% crystalline silica as 10 mg/m^3 for the inhalable fraction (<100 μm) and 3 mg/m^3 for the respirable fraction (<4 μm). OELs in the U.K. are similar to those in New Zealand: exposure to inhalable dust should not exceed 10 mg/m^3 over an 8-hour period and exposure to respirable dust should not exceed 4 mg/m^3, irrespective of the crystalline silica content. In instances where there is evidence of hazards to health below these given levels, exposure should be controlled accordingly (Health and Safety Executive, 2008). In Canada, OELs are set by agencies in regional offices (Canadian Centre for Occupational Health and Safety, 2012). Montserrat as a British Overseas Territory should follow the HSE guidelines of the UK; however, quarry employees were unaware of any guidelines or OELs regarding dust hazard from quarrying.

In Europe, the Chemicals Working Party advises the European Commission on OELs according to health-based limits set under the Chemical Agents Directive (98/24/EC).

Currently, new policy for the regulation of crystalline silica is being prepared: recently the Chemicals Working Party (2012) recommended that respirable crystalline silica not maintain its current listing within the Carcinogen Directive and called for a binding European OEL of 0.1 mg/m³ to avoid penalising industrial sectors where exposure exists but silicosis hazard does not, and that only specific processes handling respirable crystalline silica be regulated at EU level. Figures for permissible levels of workplace dust exposure vary somewhat among countries. This is probably due to the fact that there is no 'absolute' threshold above which exposure is dangerous and below which exposure is safe. Table 6.2 summarises the details for legislation governing occupational exposure to general dust and crystalline silica dusts for a selection of countries, including: the UK, other European countries, New Zealand and the U.S.A.

Evidence of hazard in an occupational setting is transformed into exposure levels following a combination of scientific, social and economic factors, broadly encompassing: research published, lobbying groups and feasibility considerations within the industry (Verma *et al.*, 2002). Further details are presented in Table 6.3 which illustrates the types of evidence used to determine occupational health issues and the factors that influence the design of exposure levels and associated controls.

Table 6.2 Maximum permitted OELs, based on 8-hr TWA for respirable dust in various European countries, the USA and New Zealand: n/a not applicable; *Germany no longer uses OEL for crystalline silica (employers must minimize exposure as much as possible instead); § Figure for inhalable dust; +USA calculates SiO2 exposure: 10 mg/m3 divided by (%SiO2+2). Fieldwork was conducted in countries highlighted in red. Compiled from Eurosil (2010), NZ Department of Labour (2011), US Department of Labor, Occupational Safety and Health Administration (2008).

Country	Total Respirable (Inert) dust mg/m^3	Quartz mg/m^3	Cristobalite mg/m^3	Tridymite mg/m^3
Austria	6	0.15	0.15	0.15
Belgium	3	0.1	0.05	0.05
Bulgaria	4	0.07	0.07	0.07
Czech Republic	n/a	0.1	0.1	0.1
Denmark	5	0.1	0.05	0.05
Estonia	n/a	0.1	0.05	0.05
Finland	n/a	0.05	0.05	0.05
France	5	0.1	0.05	0.05
Germany	3	*	*	*
Greece	**5**	**0.1**	**0.05**	**0.05**
Hungary	n/a	0.15	0.1	0.15
Ireland	4	0.05	0.05	0.05
Italy	3	0.025	0.025	0.025
Lithuania	10	0.1	0.05	0.05
Luxembourg	6	0.15	0.15	0.15
Netherlands	5	0.075	0.075	0.075
Norway	5	0.1	0.05	0.05
Poland	n/a	0.3	0.3	0.3
Portugal	5	0.025	0.025	0.025
Romania	10	0.1	0.05	0.05
Slovakia	n/a	0.1	0.1	0.1
Slovenia	n/a	0.15	0.15	0.15
Spain	3	0.1	0.05	0.05
Sweden	5	0.1	0.05	0.05
Switzerland	6	0.15	0.15	0.15
United Kingdom	**4**	**0.1**	**0.1**	**0.1**
New Zealand	**3**	**0.2**	**0.1**	**0.1**§
United States	5	+	+	+

Table 6.3 Types of evidence used to inform occupational exposure controls and the factors which influence them. After Veerma et al., (2002).

Source	Evidence Type	
Toxicology	Causal agent	
	Dose–effect/response data	
	Toxicity and disease mechanisms	
	Candidate biomarkers for biological monitoring	
Epidemiology	Causal agent/process	
	Exposure–effect/response data	
	Validation of biomarkers for biological monitoring	
Occupational Medicine	Clinical observation of disease from routine or specific medical surveillance	
Occupational Hygiene	Exposure measurements in comparison to control limits	
Unions/Workers	Reports of complaints or ill health among workers	
Scientific/technical	**Social**	**Economic**
Strength of scientific evidence. Ongoing research. Control options: - Availability - Technical feasibility Information: - Availability - Generation and dissemination Suppliers' material safety data sheets and labels. Availability of occupational hygiene professionals.	Nature of disease. Human cost. Public perception. Media interest. Business (labour relations). Influence of unions/business on government. Philosophy of government.	Cost of control options. Impact on industry. Effect on competitive advantage. Trade agreements. Suppliers' material safety data sheets and labels.

6.2 Aims and Hypotheses

Whilst it is clearly important to ascertain the physiochemical parameters which govern the respirable hazard of dust particles, it is equally important to determine the concentration of respirable dust in the air and which factors control exposure to these dusts. The overall aim of this chapter is to determine the differences in exposure that arise from quarry workers fulfilling different occupational roles. The specific hypotheses used to investigate these factors are as follows.

1) *The ambient concentration of quarry dusts differs depending upon the type of deposit being quarried and the site within the quarry.*

The grain size analysis (as detailed in Chapter 4) of bulk samples revealed differences in the quantity of respirable material depending on the type of deposit being extracted and on the extraction and processing techniques being applied. This chapter addresses whether ambient, airborne dust follows this pattern, with dust concentrations varying according to location within the quarries, as well as to the type of deposit.

2) *The personal dust exposure of quarry workers differs depending on their particular role within the operation.*

Quarry workers often have a specific task which they repeat throughout their shift; therefore, they are likely to be exposed to semi-consistent levels of dust each day (depending on weather variability). The nature of tasks within a quarry differs and therefore the associated exposure is likely to be task-dependent. As some workers are likely to be exposed to higher levels of dust than others, they may require greater protection. This chapter thus investigates whether personal exposures can be linked to specific tasks. The results may allow specific tasks to be designated as more hazardous for the benefit of exposure management.

3) *Mitigation and management of dust as a hazard differs amongst quarries on both a corporate (management) and individual (worker) scale.*

Legislation regarding occupational exposure to dust varies amongst countries and it is likely that the method of dust management and mitigation will vary, not only between country borders but also amongst different quarries in the same country. Such variations are likely to result from: specific differences in quarry operation (e.g. types of extraction and processing methods), differences in corporate style (between large multinationals and independent companies) and differences in individual risk perception (where RPE is optional rather than mandatory). In this chapter, management of dust hazard is assessed through ethnographic observations supported by limited questionnaire-based surveys.

6.3 Methodology

Air quality monitoring was carried out at chosen quarries which covered a range of magma and deposit types, and quarrying activities (see Chapter 3 for specific quarries and their locations). For the mafic quarries, three were chosen that had active extraction and processing operations. For the intermediate quarries, the sites on Montserrat were subject to controls following the extension of the volcanic exclusion zone one week before the field campaign commenced in January 2010. The only area where active movement of quarry material was allowed was at Little Bay, which was the location of the Pheonix quarry and, also, where a small block factory used material from Trants to make breeze blocks, and where Eddie's trucking (which extracted material from Trants) had a holding and stockpile area. Phoenix quarry typically extracted material from a cliff face of ancient PDCs in Little Bay; however, there was no extraction taking place as the cliff had not recently been inspected for stability and so was not deemed to be safe. In addition, no processing was taking place, because a part of the processor was broken. For the felsic sites, Yali was chosen (there was no active processing at the felsic quarries Atiamuri or Te Puke in New Zealand) with a greater focus on the larger pumice site compared with the smaller perlite operation. The Hunua greywacke quarry in New Zealand was included as a non-volcanic comparison, and some ash fall monitoring was also conducted in western Montserrat. Ethnographic studies (observation of quarry worker behaviours) were

conducted at all sites where airborne dust exposure was monitored; however, due to language limitations, the questionnaires were only carried out in New Zealand and Montserrat. Table 6.4 shows which types of analyses were conducted at which quarry.

Table 6.4 The types of analyses conducted and which quarries were surveyed. * The block factory was situated in Little Bay and produced blocks (at the time of the field campaign from material quarried in Trants).

Magma Type	Country	Quarry	Ambient Exposure	Filters	Personal Exposure	Dust Management
Mafic	New Zealand	Bombay	√	√	√	√
		Puketutu	√	√	√	√
		Flat Top	√	√	√	√
Intermediate	Montserrat	Eddie's	√	√	√	√
		Block Factory*	√	√	√	√
Felsic	Greece	Aegean Perlite	√	√	√	√
		LAVA pumice	√	√	√	√
Non-volcanic greywacke	New Zealand	Hunua	√		√	√

6.3.1 Ambient Dust Concentration

Commonly-used gravimetric and photometric methods were employed to measure the concentrations of ambient airborne dust. The former involves measurement of a mass of sample collected over a given time, whilst the latter involves real-time continuous measurements. For this study, a Sioutas personal cascade impactor (CI) was used for gravimetric collection and a TSI DustTrak aerosol monitor (model 8520) for photometric monitoring.

6.3.1.1 Gravimetric Collection of Dust

The Sioutas CI collects particles of different sizes onto filters housed within its casing; the size cut-offs are for particles 2.5 µm, 1.0 µm, 0.50 µm, and 0.25 µm across. The air is pumped into the impactor by a Leland Legacy Pump which is set to a flow rate of 9 L/minute. The size-fractionated dust was collected on polycarbonate filters. The mass of dust collected was determined from the difference in the weight of the filters before and

after use in the field. High-precision scales were used in a clean laboratory at a constant temperature and, to minimize any affect of humidity on their weight, the filters were conditioned in the balance room for at least 24 hours before each measurement. The Sioutas CI was only used in field campaigns in Montserrat and Greece, because appropriate facilities for filter weighing were not available at the time of the New Zealand campaign.

6.3.1.2 Photometric Monitoring of Dust

The DustTrak is a light-scatter laser photometric monitor which can measure concentrations of one size fraction of interest. The instrument takes in particle-laden air through a size-selective inlet and the internal light scattering is directly proportional to the concentration of dust of the designated size. Data are averaged over each minute of collection time and a reading is recorded every 10 seconds. The instrument is factory calibrated according to ISO (International Standards Organisation) 12103-1, which is an Arizona road dust similar to volcanic ash, and an in-field zero-calibration was conducted prior to each use.

Where work shifts were split into two (e.g. before and after a lunch break) the aggregated data were compiled for an 8-hour TWA, using the following equation:

$$8\ hr\ TWA = \frac{(x_1 \times y_1)+(x_2 \times y_2)}{8} \qquad \textbf{Equation 6.1}$$

where x and y are the number of hours and the level of exposure, and the subscripts identify the first and second shifts.

6.3.1.3 Sites of Ambient Dust Collection and Monitoring

Ambient dust locations were selected in order to represent the 'background' levels of dust to which workers (of various roles) may be exposed by passing through different areas of a quarry. Both the DustTrak and Sioutas instruments were used in tandem. Rather than repeated sampling at one location within one quarry, a broad overview of exposure within different quarries was obtained. As described in Section 3.3, the layout of

most of the mafic quarries and the greywacke quarry at Hunua could be divided into three areas: for blasting and excavation, for processing, and for stockpiling (Figure 6.2).

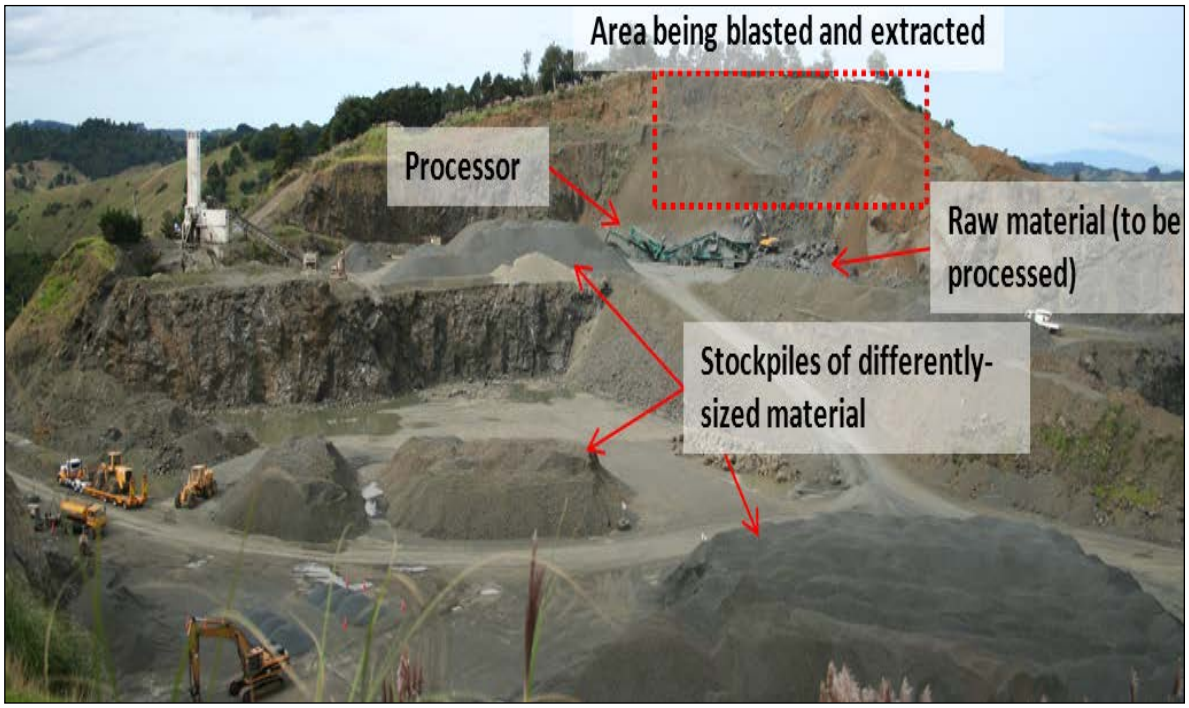

Figure 6.2 Flat Top quarry in New Zealand with typical features marked. The quarries at Bombay, Puketutu and Hunua (all New Zealand) shared these features and had a similar layout.

Monitoring at the mafic quarries was conducted at the blast site (during blasting), along roadsides (either between the pit and the processor or near the stockpiles where processed material is deposited) and near the processor (where crushing and screening take place). For the intermediate quarry at Little Bay, the monitoring locations were inside the block-factory shed, at the side of the dirt road, and in the Eddie's trucking holding area. At the felsic quarries on Yali, monitors were installed in the stockpile tunnels, by the processor and in the mechanics yard.

In the mafic and greywacke quarries, the blast site may not be considered an 'ambient' location (blasting is a regular, but not a constant activity); however, it was included because, at almost all the quarries, workers were present during the blast (at a safe distance of about 100 metres). The sole exception was Flat Top quarry, where everyone on site (except for the person igniting the explosives) had to wait in a shed on the edge of the site, around 500 metres from the blast. Excavation and removal (to the processor) of blasted material took place as soon as the blasting team deemed it safe (once they had checked there would be no further collapse). This was often 20-30

minutes after the blast and whilst the cloud of dust and explosives was still visible in the air; the blast site was therefore an area of activity shortly after the blast. Blasting is a regular occurrence at quarries (recurrence depends on size of blast and speed of processing, but every few weeks was the observed average). Monitoring of a blast is shown in Figure 6.3. In two quarries (Flat Top and Hunua) the measurement period of blasting lasted a whole shift of approximately 8 hours. In the remaining quarries the blast monitoring took place over half a shift or less, because the monitoring instrument needed to be re-located to collect measurement in other parts of the quarry (in order to obtain a full picture of exposure around different parts of each quarry). In all cases the instrument was within 50 m of the blast site, which is as close as the shot firers deemed safe.

Figure 6.3 DustTrak location during a blast at Bombay quarry, New Zealand (location of DustTrak indicated by red circle). inset: looking down onto the blast site (prior to blasting) from the DustTrak location. The explosives can just be seen in the midground (indicated by bright pink dots on dark grey surface).

At Little Bay on Montserrat, quarrying activities during the field campaign were restricted to the movement of stockpiled material by truck along a single road between the Phoenix quarry and the coast (Figure 6.4). Monitors were therefore located at selected locations along the road, at the Phoenix quarry, next to Eddie's stockpile, by the block factory and

at the coastal end of the dirt road, where it met the tarmacked surface leading to the port (Figures 6.4 and 6.5).

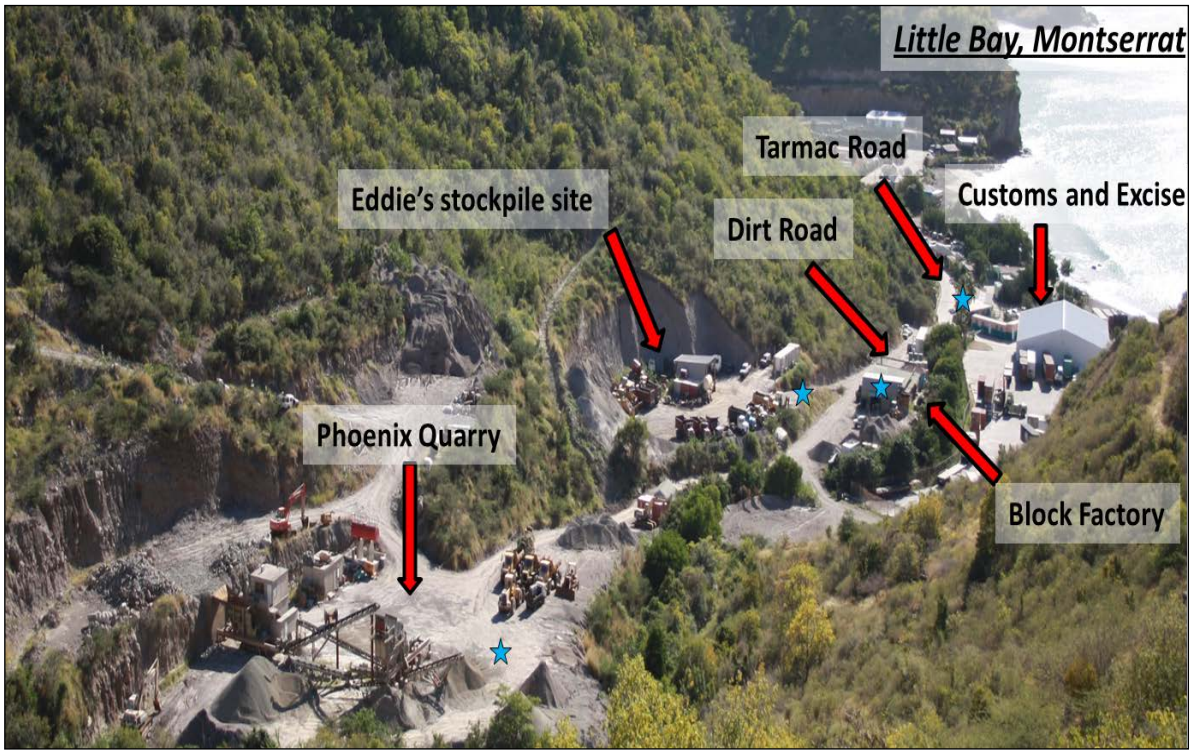

Figure 6.4 The Little Bay site in Montserrat with different areas marked. Blue stars indicate the sites at which dust monitoring took place.

Figure 6.5 DustTrak (in foreground of both images) locations at Little Bay in Montserrat. Left: near Eddie's trucking stockpile site (block factory seen to the right of the photo) and right: where the quarry dirt track meets the main tarmac road towards the jetty (an open-top truck carrying material from Eddie's to a ship, can be seen in the left of this photo).

The ambient exposure to volcanic ash was measured (during January 2010) at several locations in western Montserrat, centring on the areas of Salem and Woodlands (shown in Figure 6.6). These measurements incorporated episodes of ash fall events (during collection periods around Salem clinic) and periods without ash fall, which occurred during measurement at the checkpoint and near the school. These areas, however, had ash on the roads which was re-suspended by passing vehicles. This is a useful comparison to make with quarrying exposure and to show what levels of non-occupational exposure quarry workers might receive.

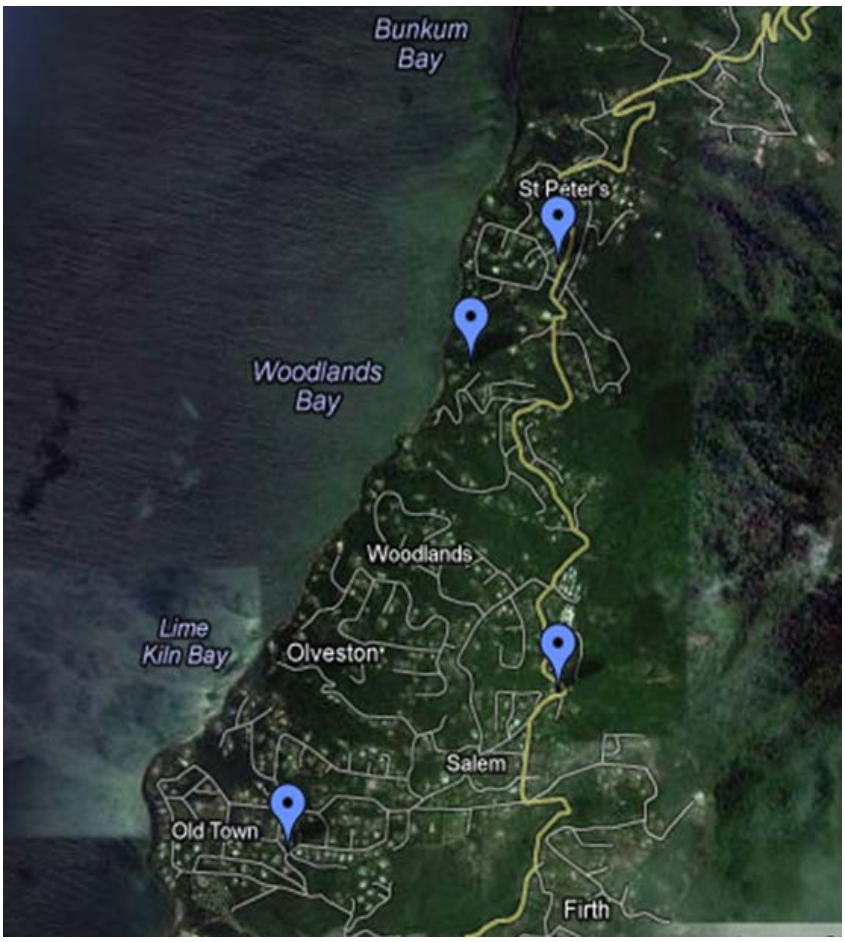

Figure 6.6 The location of ash fall and ambient monitoring in western Montserrat. Markers show (North to South): St Augustine school, Woodlands (villa), Salem Clinic, and the Checkpoint on the border between exclusion zones A and B in Old Town. Source: Google Earth (2012).

Unlike the quarries in New Zealand and on Montserrat, no roads have been constructed around the quarry on the private island of Yali, because the pumice being extracted is so soft and loose that it can only be crossed without sinking by vehicles with caterpillar tracks. As a result, the material is not moved around the quarry by trucks, but

is transported along conveyor belts (see also Figure 3.22 in Chapter 3). Monitoring stations were thus established across the LAVA pumice quarry near the processor, processor control tower, the tunnel traversed by the conveyor belt and the mechanics site where repairs take place (Figure 6.7). Additional monitors were also installed at the processing site of the neighbouring Aegean Perlite quarry (Figure 6.7).

Figure 6.7 Yali island, with locations of dust monitoring marked: 1) LAVA processor 2) LAVA tunnel 3) LAVA processor control tower 4) Aegean Perlite processor; 5) LAVA mechanics site.

6.3.1.4 Field Methodology for Ambient Dust Collection and Monitoring

Measurements of both PM4 (particulate matter <4 μm) and PM10 were taken at the mafic and intermediate quarries of New Zealand and Montserrat and run for one day at a time within their specific location. These fractions were chosen because they represent the international standards of thoracic (PM10) and respirable (PM4) material in accordance with the ISO health-related particle size sampling convention ISO7708 (1994) (Quality of Urban Air Review Group, 1996); see also Chapter 2 Figure 2.3) as used in monitoring with the standard 50% cut-off size for respirable aerosol mass. Measurements of PM4 were taken with a cyclone attachment fitted, to adjust the flow rate and achieve the respirable cut-off. This works by forcing the dust-laden air to swirl inside the body of the cyclone so that larger particles unable to follow in the air stream become trapped in a grit pot, whilst smaller particles stay in the air stream and pass through the instrument and are detected photometrically. As the field campaign on Yali was only 5 days long the instrument was set only to PM10; the instrument set-up in the field is shown in Figure 6.8.

Figure 6.8 DustTrak and Sioutas on the processor at LAVA quarry, Yali. The instruments were always mounted at adult breathing level (1.5-2m off the ground). Inset: positioning of instruments on processor platform, but in breathing zone of the path next to the processor.

Monitoring times varied in New Zealand as each day's measurement and instrument location had to be approved by the manager depending on the particular activities and their locations on the day. In Montserrat, there were some days where there was no activity on site and other days when there were only a few hours (sometimes less than half a day). The only times where a full day (>6 hours) of activity ensued was when material was being moved out of Little Bay and onto a ship. On Yali, it was possible to monitor more fully a whole shift, again after negotiation with the manager and because the author was based on site.

During the time of measurement, activity around an instrument was recorded at minute intervals in order to determine whether some specific activities or events could be identified as causing particular fluctuations in the dust levels. Instrumental readings were repeated whenever possible. However this was not always feasible given time constraints during the field visits. For all data, averages were calculated for each run and, for comparison with OELs, an 8-hour TWA calculated to give the average exposure over an 8-hour shift.

Local meterological conditions were noted as part of in-field observations and wind strength was estimated using an improvised windsock (a ribbon hanging from the side of the DustTrak). A 'strong breeze' was defined on the basis of the sock's position as being >45° perpendicular to the vertical position of the DustTrak. Some larger quarries in New Zealand had their own meterological stations, so that temperature and pressure could be recorded directly; otherwise, data were obtained from local radio reports.

Inter-seasonal changes were not experienced, owing to the short duration of the field campaigns. It was not possible to obtain details of air pressure on Yali or Montserrat, because neither had monitoring stations and they are too remote to be included in observations made at neighbouring islands. Although it was difficult to account for the precise impact of weather patterns on dust levels, details of rainfall and wind, together with their potential impact, are noted where the relevant results are discussed and also feature in the evaluation of limitations and challenges in Section 6.5.2.

6.3.2 Personal exposure dust concentration

Personal exposure monitoring was conducted to ascertain differences in the exposure experienced by workers of differing roles. Exposure was measured with a TSI SidePak photometric monitor, which works in the same way as the DustTrak monitor, but is smaller and more portable. 6.3.2.1 Personal Photometric Monitoring by Quarry Role

To monitor exposure experienced by workers with different roles, several positions were selected including: foremen (with varying tasks throughout the day), vehicle drivers (both front loaders and truck drivers) and those who conducted maintenance (for example on the processor).

6.3.2.1 Field Methodology for Personal Dust Monitoring

The SidePak monitor was fitted onto the belt of the worker, with a tube attached to the lapel of the worker's shirt or overall, so that air was extracted from near their breathing zone, within 30 cm of the face (Figure 6.9).

As with the DustTrak, this instrument was set to both PM10 and PM4 (the thoracic and respirable fractions), and each worker wore it for two runs at either size cut-off. Those workers who smoked were excluded from participation as it is very difficult to avoid cigarette smoke from contaminating the exposure reading. The instrument was turned off whilst the worker went for their break, because smoking was allowed near the break room; however, data were compiled from a whole shift to determine daily exposure. Personal exposure was measured in a manner comparable to the methods employed by the UK Health and Safety Executive for assessing occupational exposure (Health and Safety Laboratory, 2000).

Figure 6.9 SidePak in-situ on a maintenance worker at LAVA quarry in Yali.

6.3.3 Observations of Dust Hazard Management

A preliminary study into dust hazard management was carried out comprising ethnography and questionnaires. Ethnographic research in the field observes groups of people as they perform the tasks that make up their daily lives (Emerson *et al.*, 2011). Data were recorded through notes and photographs and particular attention was paid to the provision of health and safety advice within quarries and to the practice of protection from dust (both quarry-wide and individual). The results are presented thematically in Section 6.4.4.

Questionnaires to explore risk perception were also undertaken with workers in New Zealand and Montserrat, but not at the quarry in Yali owing to the lack of English speakers. The results are presented in Appendix IV. Although the pilot study was too small for the results to be used to inform policy decisions, the data nevertheless provide a basis for designing an in-depth study, as discussed in Chapter 8.

6.3.4 Limitations and Challenges in Exposure Monitoring

At each quarry, dust-monitoring data were obtained primarily to investigate the exposure of workers and how this varies with their job roles and with the levels of quarrying activities. Data were obtained over intervals from 1-8 weeks. Although these provide a basis for investigating the relative exposure of workers in different roles, they cannot easily be extrapolated to evaluate average exposure over long intervals (such as a year) at a given quarry, or to compare long-term differences between quarries. The influence of six factors are particularly difficult to quantify (Table 6.5; (U.S. Environmental Protection Agency, 2004)): weather and seasonality, type of vehicles, speed of vehicles, methods of suppressing dust, natural variations in deposits, and economic factors.

Table 6.5 Examples of some variables and their associated effects upon dust emissions

Variable	Examples and Effects
Weather and Seasonality	Rainfall, temperature, wind, humidity and air pressure can all have an impact upon dust levels. Seasonal patterns can vary throughout the year so that dust levels may not be uniform year-round.
Type of vehicles	Vehicles of different sizes and shapes have a differing impact upon dust re-suspension.
Speed of vehicles	Faster vehicle speeds create greater quantities of re-suspended dust.
Use of suppression methods	Dust suppression methods such as a water cart will impact dust levels but may not be used regularly.
Natural variations in deposit	Quantities of dust arising from crushing and processing can vary with the nature of the rock being processed e.g. mineralogical variation can result in changes to moisture content, brittleness.
Economic factors	The local demand for quarried aggregate often drives the level of extraction and processing which take place at a quarry.

As described below, even though the potential impact of each factor has been recognised at least qualitatively, the uncertainty and variability of the level of impact has hindered the development of fully-quantitative evaluations.

Weather and Seasonality

Changes in weather patterns can have a significant impact upon dust levels in a quarry. High wind speeds can provide the energy required to suspend loose particles away from the ground, with higher winds creating more dust (Appleton *et al.*, 2006), while associated turbulence can loft them into the air (Watson *et al.*, 2000). Rain adhering to quarry dust particles will increase their mass and water surface tension decreases their ability to become suspended and transported. Cohesion among wetted particles favours the formation of dust aggregates and of surface crusts that can persist after the rain has evaporated, so that the dampening of dust levels in a quarry can continue for days after the rain has stopped (Watson *et al.*, 2000). Such dampening, however, is likely to be offset by the movement of trucks breaking the aggregates and crusts on haul roads. Dust dispersion also tends to decrease with increasing humidity, which in turn is a function of air pressure and moisture (Okawa *et al.*, 2012).

The changes in weather patterns need to be accounted for during sampling so that a bias is not introduced because some sampling may have occurred, for example, during a week with sunshine, no rain and high winds, which would give much higher dust levels compared with sampling during a week with heavy rain and no winds. Changes in weather patterns also occur seasonally and, in the case of the sites studied here, the average dust levels are not expected to remain uniform all year.

The weather at Yali is fairly stable and benign. Storms are rare and typically occur only in winter. However, as the island is closed for quarrying for the whole of December, it is unlikely that workers will experience many storms, so that average conditions during quarrying are expected to be dry with a light sea breeze. The tropical climate on Montserrat produces hot and dry conditions with occasional convectional afternoon rain that can sometimes be heavy. A hurricane season typically runs from June to November, during which winds and rain are strong and frequent. Between 1995 and 2001, the frequency of storms and hurricanes increased five-fold, a trend that may continue under

expected changes in global climate (Goldenberg *et al.*, 2001). The sampling period for this study was outside of the hurricane season and therefore conditions were not representative of an annual average. In New Zealand, inter-annual variations in climate are strongly influenced by the Southern Oscillation (SO; (Gordon, 1986)). SO events increase temperatures, especially in the autumn and spring, with a weaker association February-March (Gordon, 1986). The local effects of such influences are likely to be complex as New Zealand's variable orography gives distinct regional responses to variations in atmospheric circulation (Salinger & Mullan, 1999). It is important therefore to obtain year-round measurements of exposure in order to account for any seasonal anomalies and reduce averaging bias.

Type of Vehicles

The re-suspension of dust by passing traffic is commonly related to the contact of vehicle tyres with the road surface. The tyres apply a shearing force that re-suspends particles. The shape, speed, weight and number of wheels of vehicles on quarry road surfaces therefore affects the size of dust particles, the surface loading, wind effects and surface moisture (Watson *et al.*, 2000).

However, the shape of a vehicle also affects the quantity of dust re-suspension. From laboratory experiments using ideal geometries to model the shapes of vehicles, Mollinger et al. (1993) found that, for the same basal widths and lengths, velocity, and height above the ground, the amount of dust re-suspended increased by almost a factor of 2, from about 55% to 92%, for respective changes in vehicle shape from an elliptical cylinder (with an elliptical base and circular ends) to a rectangular block. The experiments also indicated that, for similar vehicle shapes and widths, longer vehicles tend to cause a greater amount of re-suspension.

Although caution must be applied when extrapolating the absolute values in re-suspended volumes from the laboratory to the field, the experimental results reveal that vehicle shape, as well as tyre contact, can have a significant influence on dust re-suspension. During observations at the monitored quarries, the dumper trucks transporting material were essentially rectangular blocks and the water carts cylinders. Vehicles with additional geometries were also used outside the observing period, especially drill rigs and rippers prior to a blast, front loaders and dumpers after a blast,

and vehicles for general maintenance. Even with the same degree of tyre contact, therefore, levels of exposure may fluctuate according to the size and shape of the vehicles being used on any given day.

Speed of vehicles

As the speed of a quarry vehicle increases, it can re-suspend a greater quantity of dust and loft it to higher levels above the ground (Appleton *et al.*, 2006, Thompson & Visser, 2001). For safety reasons, the speed of vehicles in a quarry is typically quite slow and the maximum speeds observed at Montserrat and New Zealand were 20-30 km/hr. Such speeds are useful in keeping down dust levels, but, as observed on Montserrat when material was being shipped out, during times when large quantities of material need to be moved, economic pressure may necessitate a reduced transportation time and, hence, an increase in working speed.

Use of dust suppression methods

The use of water to suppress dust can significantly reduce the amount of dust re-suspended by moving vehicles. A surface moisture content of >2% has been shown to reduce PM10 levels by >80% compared with a surface moisture content of only 0.56% (Watson *et al.*, 2000). As a result, a water cart is typically used on dry days to moisten the dust on road surfaces. Too much watering, however, can have a detrimental effect. It can cause dust to adhere to surface of vehicles and be transported elsewhere (a phenomenon termed “carryout”), where it is deposited as it dries and so potentially can be re-suspended far from its point of origin. At Flat Top quarry (New Zealand) a washer system was in place to clean vehicles exiting the quarry site, but such a practise was not observed elsewhere. It is typically the Manager or Foreman who decides whether the water cart should be used and with what frequency. As the use is based upon an individual’s judgement rather than a prescribed set of parameters (e.g., wind levels or when it last rained), there is likely to be variation in the use of the water cart which may also affect representative sampling (especially if weather conditions are similar over a number of days and the water cart is deployed on some days but not on others).

Natural variation in the deposit

The mineralogical variation within a deposit can be subtle but may have some impact upon the dust generated during its extraction and processing as both the rock type and its associated moisture content can have an impact upon emissions during crushing (U.S. Environmental Protection Agency, 2004) with a positive correlation between the strength of the source rock and the quantity of dust generated (Bohloli & Hoven, 2007). This potential natural variation was addressed here by sampling within a range of different locations at each quarry, further repeat measurements at the same locations would further account for any potential variations.

Economic factors

Economic factors can also be a source of varying dust hazard within a quarry, particularly at locations where material is shipped. The logistical company bears a cost for each day that a ship spends docked and being loaded with quarry material; therefore the quarry companies are usually under pressure to load material as fast as possible. This was observed at both Montserrat and Yali.

In Montserrat, quarry workers arrived at work in anticipation of the ship docking and, when it arrived, they transported the stockpiled material in a single shift; this meant that they often worked late into the night far beyond their typical shift hours. In one extreme example from Eddies quarry, after all the material had been loaded, space was still available on the ship and so the manager bought the stockpile from the adjacent block factory and transported that as well. Hence, on days when material is being exported, the levels of activity within the quarry area are much higher compared to days when material is only sold locally.

In Yali, the automated system of belts means that a ship can be loaded with material (either freshly processed or from stockpiles) around the clock. Although this does not directly involve additional quarry vehicles, it may induce an increased exposure for workers near the stockpiles and belts due to extended working hours (over-night loading necessitates for 1-2 workers to remain on-site at all times).

In New Zealand, the quarries which were thriving economically had a similar level of extraction and processing on a daily basis in order to meet their monthly quotas of the minimum amount of aggregate produced. In contrast, quarries in economic difficulty (e.g.

Te Puke and Atiamuri) had ceased active processing and stockpiled their material. With the return of more favourable economic conditions, such quarries may restart processing part-time as and when demand increases. In this case, exposure levels will fluctuate over time and will need to be accounted for when evaluating exposure averaged over a longer (e.g., annual) time interval.

6.4 RESULTS

An overview of which types of analyses were conducted at each quarry is presented in Table 6.4. The results of ambient and personal exposure, and filter data, are subsequently presented in tables and graphs, whilst dust management is demonstrated with photographs and commentary.

6.4.1 Ambient Exposure

Table 6.7 shows the ambient dust concentration (average, 8-hr TWA, minimum and maximum) in different parts of a quarry; Section 6.3.1.3 describes the sampling locations in each type of quarry and they are illustrated in Figures 6.4 and 6.7. At all the quarries the ambient exposure was very low and within international standards (for UK, Greece and New Zealand) for exposure to the inhalable dust fraction (marked in red on Figure 6.10).

The highest concentrations of PM4 at the mafic quarries were recorded near the processor, at the Bombay quarry for example, the 8-hr TWA at the processor was 0.6 mg/m^3 compared with 0.02 mg/m^3 at the roadside. In the felsic quarries on Yali, the processor also produced the most airborne particulate, at PM10 an 8-hr TWA of 0.48 mg/m^3 at Aegean perlite and 0.74 mg/m^3 at LAVA pumice, compared to 0.07, 0.15 and 0.10 mg/m^3 at the stockpile tunnel, control tower and mechanics' yard of LAVA quarry respectively. Perhaps surprisingly the blast sites (where blasting and, a short while later, extraction takes place) were the least dusty sites. Blasting at Bombay, Flat Top and Puketutu revealed 8-hr TWA levels of PM10 of 0.01, 0.06 and 0.11 mg/m^3 respectively, with the non-volcanic comparison blast at Hunua giving a similar figure of 0.02 mg/m^3

The most variable dust levels were experienced at roadsides, ranging from 0.01 mg/m^3 (a wet day at Hunua) to 1.4 mg/m^3 (at Little Bay). Again the level could vary quite substantially within one location, as the roadside by Eddie's trucking had an 8-hr TWA of 0.05 mg/m^3 whilst the same road further down (approximately 10 metres) gave an 8-hr TWA of 1.4 mg/m^3 although it is important to note that the 2^{nd} figure was recorded on a day when material was being shipped out and all of the stockpiles at Eddie's were cleared by open top trucks which passed along the road to the jetty over a 10-hour period.

Table 6.6 Ambient dust concentration (PM10 and PM4) in different parts of the quarries. * Saturday (little processing as low staff and half day). § Very heavy rain.

Quarry		Date	Location	Size	Duration	Average (mg/m^3)	Maximum (mg/m^3)	Minimum (mg/m^3)	TWA (8 hr.) (mg/m^3)
Mafic	Bombay (NZ)	23/02/09	Blast site	PM10	03:57	0.008	0.094	0.004	0.008
		04/03/09	Roadside	PM10	07:00	0.308	4.129	0.010	0.308
		07/03/09*	Processor	PM4	03:42	0.128	1.194	0.007	0.064
		11/03/09	Roadside	PM4	07:55	0.017	1.202	0.001	0.017
	Flat Top (NZ)	05/03/09	Roadside	PM10	07:42	0.082	1.324	0.016	0.082
		10/03/09	Blast site	PM10	07:57	0.059	0.991	0.004	0.059
	Puketutu (NZ)	24/02/09	Blast site	PM10	01:17	0.108	1.813	0.003	0.108
		11/03/09	Blast site	PM4	02:35	0.070	0.328	0.013	0.070
		11/03/09	Roadside	PM10	04:53	0.102	0.947	0.011	0.102
Intermediate	Block Factory (Montserrat)	21/01/10	Production Shed	PM4	01:54	0.060	0.025	0.000	0.060
		26/01/10	Production Shed	PM10	03:25	0.173	1.469	0.023	0.173
	Little Bay	23/01/10	Road nr tarmac	PM10	06:53	1.148	10.756	0.017	1.435
	Eddie's Montserrat	14/01/10	Roadside	PM10	04:41	0.052	1.269	0.006	0.052
		15/01/10	Stockpiles	PM4	06:53	0.018	0.267	0.002	0.018
		16/01/10	Stockpiles	PM4	04:35	0.078	2.367	0.002	0.078
	Phoenix (Montserrat)	18/01/10	Stockpiles	PM4	05:17	0.008	0.628	0.001	0.006
		19/01/10	Stockpiles	PM4	04:31	0.003	0.189	0.000	0.002
Felsic	Aegean Perlite (Yali)	08/07/10	Processor	PM10	06:40	0.478	5.056	0.018	0.478
	LAVA pumice (Yali)	05/07/10	Processor	PM10	03:56	0.740	9.785	0.156	0.740
		06/07/10	Stockpile tunnel	PM10	07:18	0.074	0.528	0.024	0.074
		07/07/10	Control tower	PM10	06:16	0.147	0.765	0.020	0.147
		09/07/10	Mechanics' yard	PM10	06:30	0.097	0.444	0.026	0.097
Greywacke	Hunua (NZ)	06/03/09§	Roadside	PM10	05:40	0.009	0.073	0.001	0.009
		09/03/09	Blast site	PM10	07:20	0.015	0.195	0.008	0.015

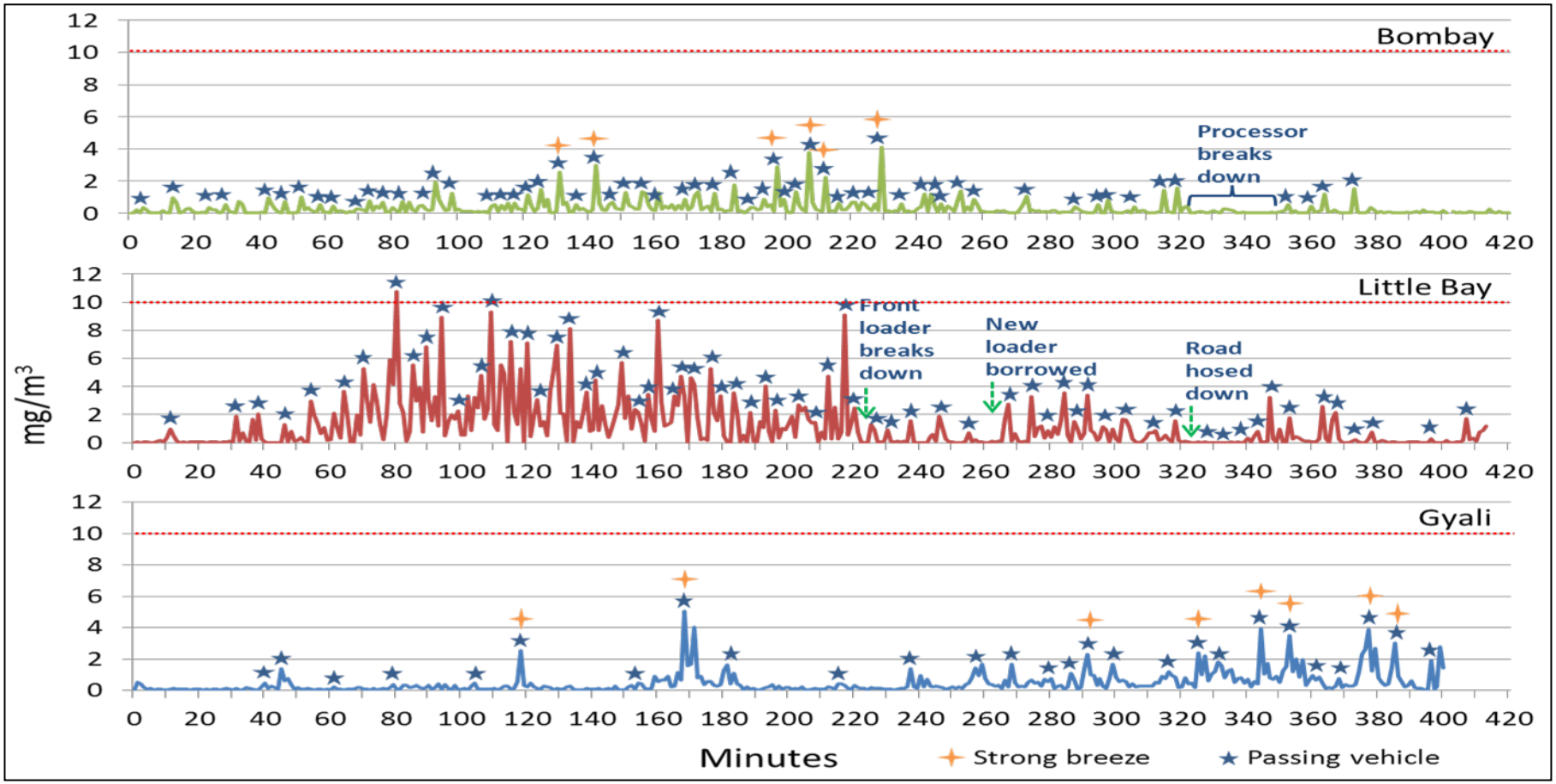

Figure 6.10 The ambient concentrations of PM10 dust at two road sides: Little Bay (intermediate) and Bombay (mafic) and a processor on Yali (felsic, perlite) with real-time annotations of accompanying activities, including passing vehicles and instances of breeze. OEL limit for *inhalable* dust marked in red.

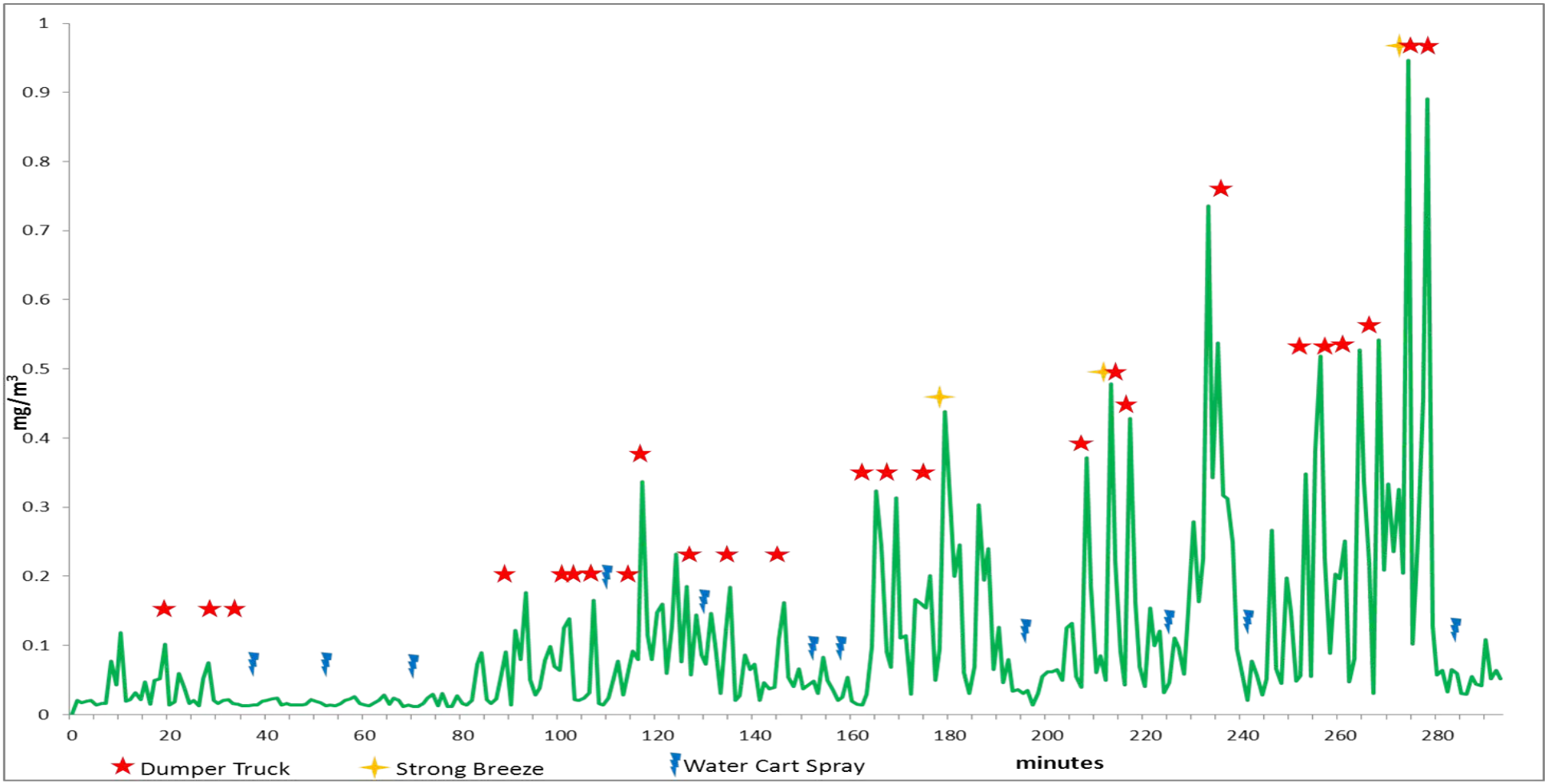

Figure 6.11 The ambient concentrations of PM10 dust along the main quarry road at Puketutu mafic quarry on 11/03/09, with real-time annotations of accompanying activities, including largest passing vehicles (dumper trucks), instances of strong breeze and spraying by the water cart.

Representative ambient air quality measurements for PM10 over a seven hour interval from a mafic, intermediate and felsic quarry are shown in Figure 6.10. The sampling sites were a roadside (at Bombay and Little Bay) and a perlite processor. Observations were noted during each minute of activity around the instrument during the time of measurement and some specific activities can be identified as causing particular peaks in the dust level. The movement of vehicles (either carrying material along the road side or delivering raw perlite to the processor) result in very distinct peaks, due both to the re-suspension of dust from the road and to the dust blown from the vehicles themselves (loaders and trucks are 'open-top' so that the transported material is not covered). These peaks usually appeared within a few seconds of the vehicle passing and therefore correlate quite clearly to within the same minute of the increased dustiness being recorded instrumentally. At two of the sites (Yali and Bombay) there was also an occasional breeze which, coupled with the movement of vehicles, systematically gave the highest readings (e.g. 5.1 mg/m^3 at Yali and 4.1 mg/m^3 at Bombay).

The highest readings at Little Bay occurred during the period when there was the greatest movement of trucks (in the first half of the period sampled). The rate later slowed after a front loader broke down (which was assisting in the movement of material from the stockpiles to the trucks) as there was then only an excavator (digger) remained available to load the trucks, until the arrival of a new loader. The passing movement of trucks transporting material can be quite regular and rhythmic (as seen in Bombay, where trucks passed every few minutes) and their absence is clearly reflected in the exposure data, such as when the processor broke down at Bombay and could accept no further material; the last few peaks are the vehicles returning to their overnight parking.

Figure 6.11 shows the ambient conditions along the main road at Puketutu basalt quarry (New Zealand) for a five hour period. The PM10 concentration is well below the OEL of 10 mg/m^3, with the highest reading being only around 1mg/m^3 and lasting barely a couple of minutes. During this period small vehicles (e.g. cars and utility vehicles) passed along the quarry road at almost every minute; however, only the dumper trucks, which are the largest and heaviest vehicles, are noted here as they are known to create the greatest amounts of re-suspended dust (Watson *et al.*, 2000). The water cart sprayed the road at fairly regular intervals (approximately every 15-40 minutes) and the effect of this upon ambient dust levels can clearly be seen on the graph as the dust levels always

decrease after the road has been sprayed; this effect is very short-lived however, and often the dust levels return to higher levels only minutes later, usually as the result of the surface of the road drying and the dust becoming re-suspended by either a strong breeze or a large passing vehicle.

Figure 6.12 shows the ambient dust levels at four quarries the basaltic Flat Top, Bombay and Puketutu and greywacke Hunua quarries when blasting took place. At Flat Top and Hunua the measurement period lasted a whole shift of approximately 8 hours; at Puketutu and Bombay monitoring continued over half a shift or less as the instrument needed to be re-located to collect measurement in other parts of the quarry (in order to obtain a full picture of exposure around different parts of each quarry). In all cases the instrument was within 50m of the blast site (as close as the shot firers deemed safe). The effects of blasting on PM10 concentrations are mixed, with a clear signal in some quarries but not in others. Bombay quarry (on 23/02/09) and Hunua quarry (09/03/09) had lower levels of PM10 (0.01-0.1 mg/m^3) but the changes caused by blasting can clearly be seen (Figure 6.12); conversely, the PM10 levels at Flat Top, Bombay (on 04/03/09) and Puketutu are much higher (0.01-1.0 mg/m^3) and the blast signal is not easily discerned from the background levels, highlighting the importance of accounting for wind speed and direction when taking measurements. The dust from blasts, however, remained within OEL levels. Where the blasting signals are discernible in the PM10 levels, the effects appear short-lived as the blast itself typically takes about a minute and the fine particles (both from drilling which remained on the surface of the rock being blasted and resulting from the blast itself when the face is blown up) soon disperse or fall to the ground. There is also the possibility that some smoke particles from the explosives fired as part of the blast, register on the instrument in addition to the rock dust .

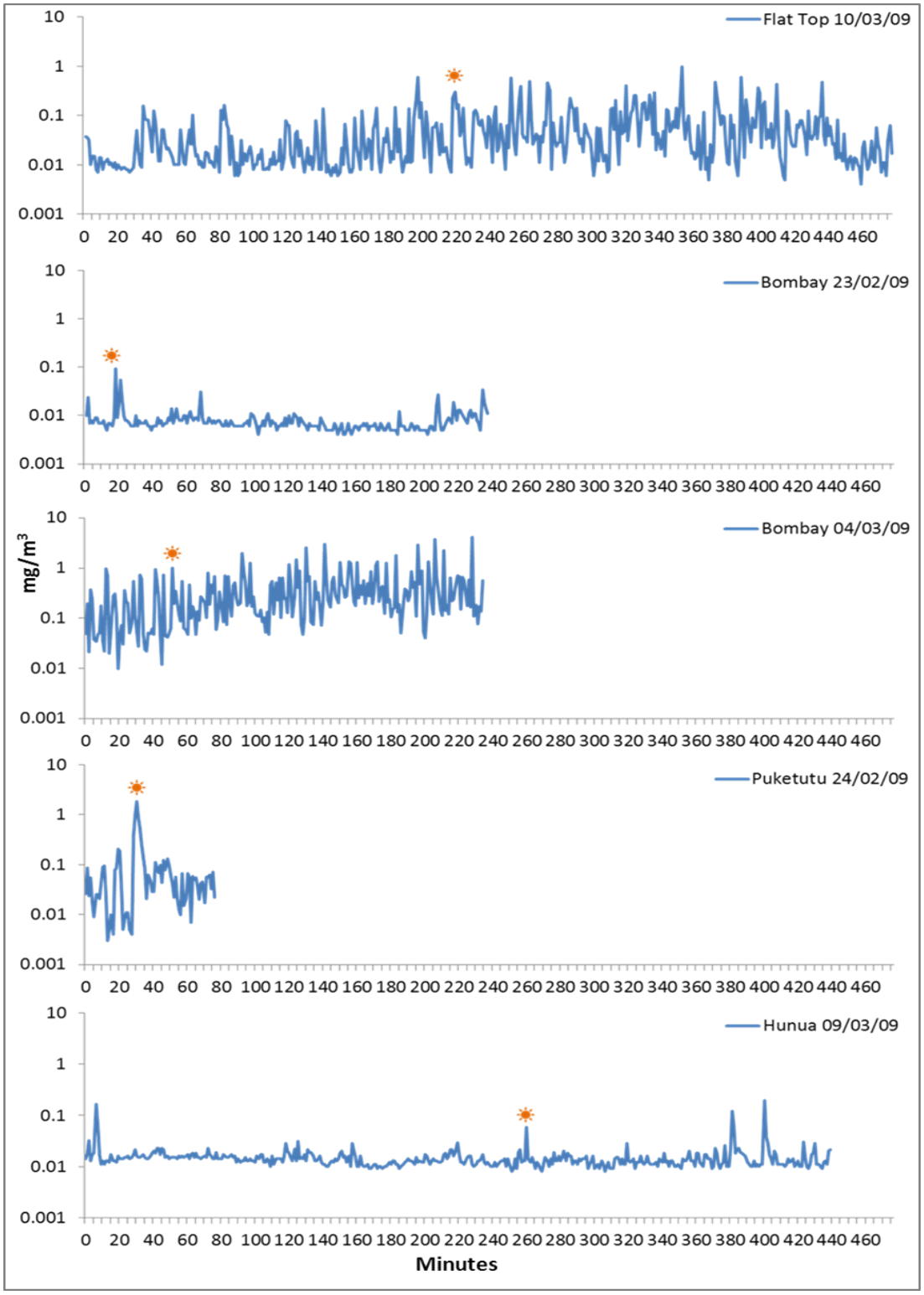

Figure 6.12 Concentrations of PM10 dust (per minute) in three basaltic quarries (Flat Top, Bombay and Puketutu) and one greywacke quarry (Hunua). Blasts are indicated with an orange sun. Note exposure scale is logarithmic to display fluctuations more clearly.

The ambient respirable fraction was also measured with filters where the material was deposited by size fraction using the Sioutas cascade impactor. This provides information on the exact break-down of the respirable fraction and how much fine material it contained. Table 6.7 shows the 8 hour TWA mass accumulation at different

sites in Little Bay and Yali. The instrument was run in tandem with the DustTrak and the 8 hour TWA calculated in the same way. At Little Bay in Montserrat, the greatest exposure was where the dirt road meets the tarmacked road leading from the quarry sites to the jetty. The exposure was measured here during the movement of material from Eddie's holding area to a ship waiting at the jetty at the bottom of the tarmacked road. The dirt road itself is naturally quite dusty (up to a total of 0.3 µm ≤ 2.5 µm) but when combined with heavy traffic (re-suspending the dirt already on the road) and open top trucks carrying material (which lofts off the piles) the dust levels soar to a total of 4.22 µm ≤ 2.5 µm.

In Yali, the dust accumulation was consistently higher, with the processor giving the highest levels (1.8 µg for the pumice processor and 2.1 µg for the perlite processor 8 hr TWA). The tunnel exit had the lowest mass (0.5 µg), and it is likely that inside the tunnel, the mass would be higher (as raw material is released onto the belt through valves in the tunnel roof) which is why masks are advised inside the tunnels (see the next section 6.4.4 and Figure 6.19). Whilst the actual weight of deposited material is extremely small, it is possible to discern differences amongst the 4 separate size fractions as shown in Table 6.7 and graphically in Figure 6.13.

Table 6.7 The dust accumulation 8 hr TWA, for different components of the respirable fraction. Sizes are: 2.5-1.0, 1.0-0.5, 0.5-0.25 and <0.25 µm

Country	Quarry & Location	Date	Accumulation in µg (8 hr. TWA) upper limit size fraction				Total
			2.5 µm	1.0 µm	0.50 µm	0.25 µm	
Montserrat	Eddie's stockpile area	13/01/10	2.165	3.681	0.650	2.093	8.589
		16/01/10	0.307	0.019	0.098	0.100	0.524
	Phoenix Quarry	18/01/10	0.008	0.051	0.131	0.003	0.193
	Block Factory	21/01/10	0.169	0.256	0.018	0.087	0.530
	Where dirt road meets tarmac road	23/01/10	0.411	1.076	2.445	2.198	6.129
Greece	LAVA: processor	05/07/10	2.557	0.700	0.165	0.330	3.752
	LAVA: tunnel exit (nr. belt)	06/07/10	0.359	0.105	0.042	0.031	0.537
	LAVA: Control tower	07/07/10	0.833	0.132	0.089	0.055	1.109
	Aeagean Perlite: processor	08/07/10	1.728	0.477	0.154	0.156	2.515
	LAVA: Mechanic's area	09/07/10	0.516	0.087	0.087	0.106	0.796

In Little Bay (Montserrat), there was variation between the two days of monitoring at Eddie's stockpile site. On the 13/01/10 the workers were not moving material but doing mechanical repairs and the largest deposition was of the 1.0-0.5 µm fraction. On 16/01/10, however, there were a lot of trucks moving material off site; the largest deposition was in the 2.5-1.0 µm fraction. The greatest amount of dust was located at the site where the dirt road meets the tarmac road, this was also the site where the DustTrak monitor detected the highest levels. In this instance, there was around 75% more material deposited in the two fractions ≤0.5 µm than the two larger fractions. This indicates that quantities of comparatively coarser dust (i.e. 2.5 µm) do not correlate with finer dusts and that it is not possible to draw inferences regarding quantities of a particular dust fraction based upon the observed quantity of a similarly-sized fraction. At Yali less variation was shown, all of the five sites measured had highest deposition at the largest size fraction (2.5 µm) as shown in Table 6.7.

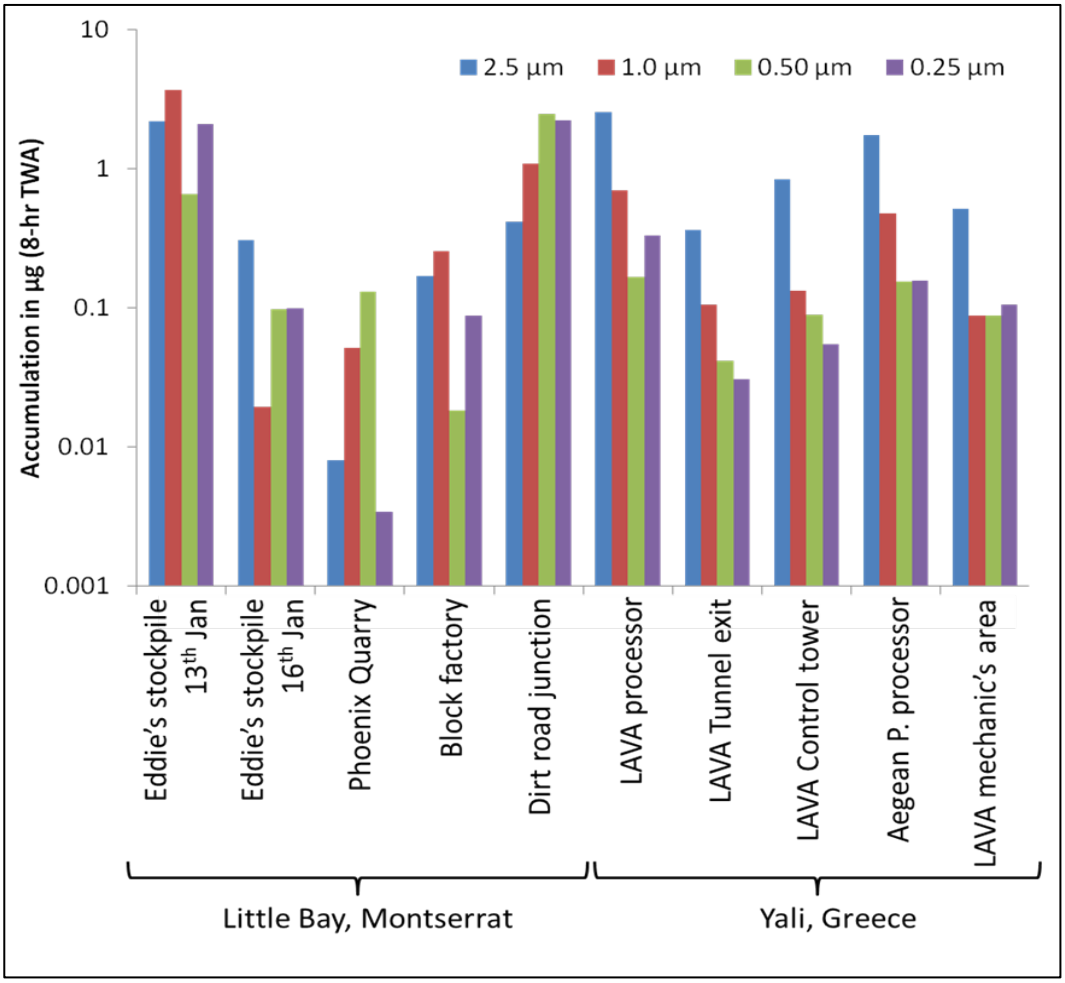

Figure 6.13 Total accumulation of dust in µg over 8 hr. TWA (upper limit size fraction) at various locations in Little Bay and Yali.

6.4.2 Personal Exposure

The personal exposure of the workers, shown in Table 6.8 was also low, with PM10 8-hr TWAs ranging from 0.02 mg/m^3 (for truck drivers in Hunua, the non-volcanic comparison) to 0.32 mg/m^3 (for maintenance workers in LAVA). Overall the felsic quarry in Yali was the dustiest place to work with all tasks giving a range of 0.2-0.4 mg/m^3 PM10 8-hr TWA. The exposure (PM10 8-hr TWA) of those in vehicle-based jobs was 0.2-0.4 mg/m^3 for an excavator and loader driver in Bombay, 0.1 mg/m^3 for a loader driver at Flat Top, 0.02 mg/m^3 for a loader driver at Puketutu (all New Zealand), 0.03 mg/m^3 and 0.07 mg/m^3 for truck drivers in Little Bay (Montserrat) and 0.4 mg/m^3 for a loader driver on Yali. In comparison, those jobs which required moving around the quarry on foot (such as a foreman, maintenance or processor workers) experienced somewhat higher exposures overall, with PM10 8-hr TWA at 0.22 mg/m^3 and 0.04 mg/m^3 for foremen (at Flat Top and Eddie's trucking respectively) 0.07 mg/m^3 for a block maker (Block Factory, Little Bay), and 0.2-0.3 mg/m^3 for maintenance workers in Yali. A similar pattern was observed for the respirable fraction, with drivers having an 8-hr TWA of 0.03-0.04 mg/m^3 (at Flat Top and Bombay) and 0.1 mg/m^3 (Little Bay), compared to 0.05 mg/m^3 and 0.11 mg/m^3 for a processor operator and maintenance worker respectively (both Bombay) and 0.04 and 0.02 mg/m^3 for a foreman and block maker (Flat Top and Block factory, respectively).

Due to the hazardous nature of quarrying it was not possible to shadow individual workers to determine the specific activities related to the peaks in their exposure However, it was observed for the Yali driver that peaks in exposure correlated with his picking up material from near the processor. The personal exposure of loader and truck drivers (PM10) is shown in Figure 6.15 for at six sites across the magmatic spectrum. Drivers at the LAVA quarry on Yali were consistently exposed to the highest levels of dust. At all the quarries, though, the levels fell well below the OELs for the individual countries.

Table 6.8 The personal dust exposure (PM10 and PM4) for different jobs within a quarry. *Occasional Saturday processing (little material processed as low staff). [+]Driver had window of truck half open. [§] Very heavy rain.

Quarry		Date	Job/role	Size	Duration (hrs.:mins.)	Average (mg/m^3)	Maximum (mg/m^3)	Minimum (mg/m^3)	TWA (8 hr.) (mg/m^3)
Mafic	Bombay (NZ)	23/02/09	Excavator	PM10	03:04	0.015	0.088	0.005	0.015
		04/03/09	Loader Driver	PM10	05:31	0.035	0.251	0.010	0.035
		07/03/09*	Processor Operator	PM4	01:38	0.099	2.326	0.017	0.050
		11/03/09	Maintenance worker	PM4	05:26	0.106	0.747	0.006	0.106
		07/04/09	Loader Driver	PM4	06:29	0.031	0.120	0.007	0.039
	Flat Top (NZ)	26/02/09	Foreman	PM10	04:48	0.173	4.472	0.006	0.216
		05/03/09	Loader Driver	PM10	03:56	0.086	0.330	0.016	0.086
		10/03/09	Loader Driver	PM4	05:35	0.027	0.169	0.004	0.027
		02/04/09	Foreman	PM4	03:46	0.035	0.391	0.007	0.035
	Puketutu (NZ)	02/03/09	Loader Driver	PM10	05:46	0.019	2.469	0.010	0.019
		11/03/09[+]	Truck Driver	PM10	06:49	0.025	0.252	0.006	0.025
Intermediate	Block Factory (Montserrat)	21/01/10	Block Maker	PM4	06:57	0.021	0.689	0.005	0.021
		26/01/10	Block Maker	PM10	03:18	0.071	0.720	0.013	0.071
	Eddie's Trucking (Montserrat)	15/01/10	Trucker	PM10	04:21	0.032	0.182	0.006	0.032
		16/01/10	Trucker	PM4	03:22	0.098	0.505	0.104	0.098
		23/01/10	Trucker	PM10	04:01	0.055	0.581	0.007	0.069
		29/01/10	Foreman	PM10	03:18	0.042	0.465	0.013	0.042
	Phoenix (Montserrat)	19/01/10	Loader Driver	PM4	00:45	0.031	0.483	0.007	0.023
Felsic	Aegean Perlite (Yali)	08/07/10	Maintenance worker	PM10	05:25	0.265	1.126	0.086	0.265
	LAVA Pumice (Yali)	06/07/10	Loader Driver	PM10	06:17	0.367	3.130	0.013	0.367
		07/07/10	Maintenance worker	PM10	05:34	0.211	1.132	0.017	0.211
		09/07/10	Maintenance worker	PM10	03:42	0.324	0.675	0.080	0.324
Greywacke	Hunua (NZ)	06/03/09[§]	Truck Driver	PM10	03:12	0.022	0.097	0.008	0.022
		09/03/09	Truck Driver	PM10	04:45	0.019	0.148	0.008	0.019

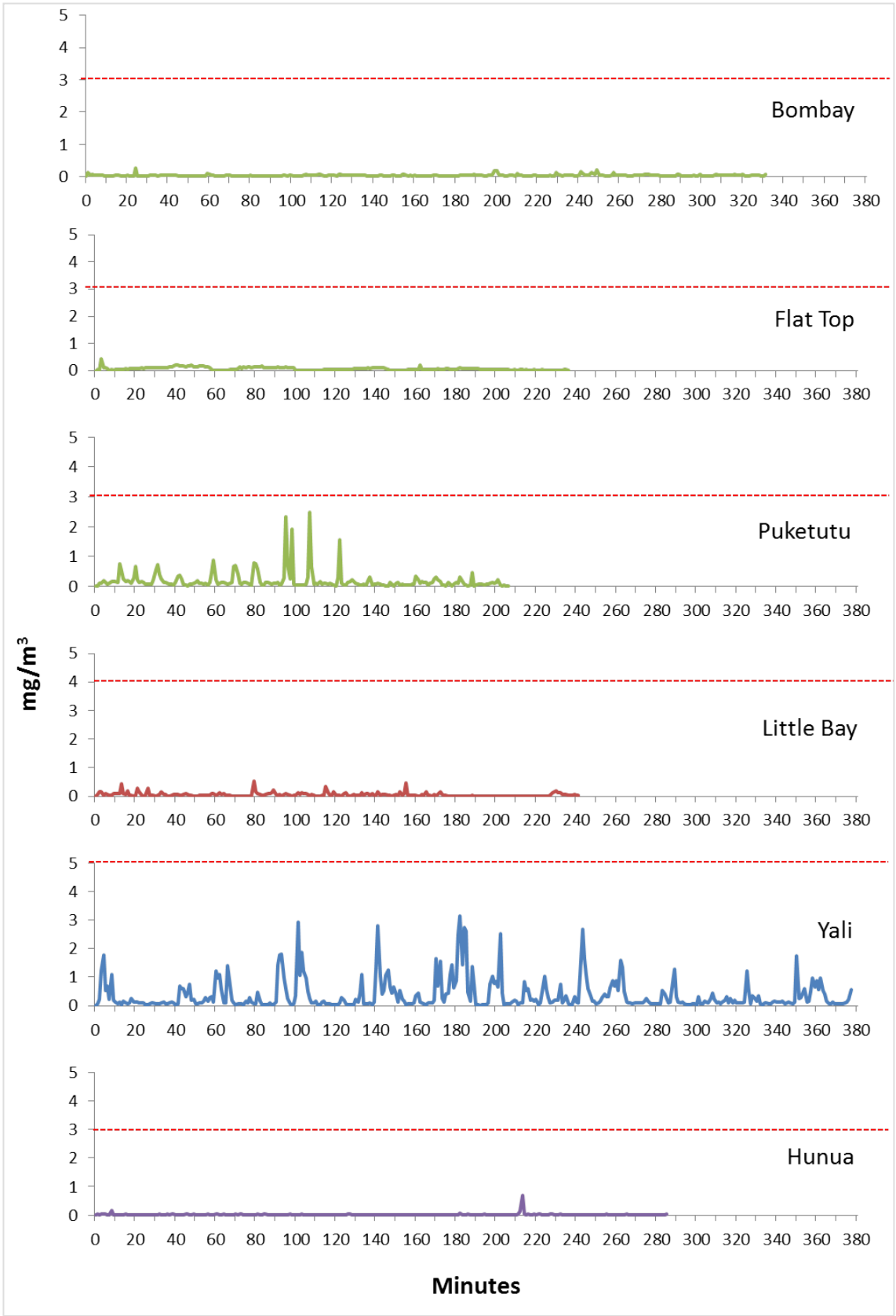

Figure 6.14 The personal exposure of loader and truck drivers PM10 dust at six sites: Bombay, Flat Top and Puketutu (Mafic, New Zealand), Little Bay (intermediate, Montserrat), Yali (felsic, perlite) and a non-volcanic comparison at Hunua (greywacke, New Zealand). The country-specific OEL to *respirable* dust is marked in red.

6.4.3 Volcanic Ash Exposure

The figures for personal and ambient exposure to volcanic ash are shown in Table 6.9 for different locations and occupations in Western Montserrat. Ambient monitoring often took place over periods longer than an 8-10 hour quarry worker shift (up to 40 hours), nevertheless the exposures were substantially less than those at the quarries.

Table 6.9 The ash exposure for PM10 and PM4 for Woodlands and Salem, both ambient top and personal bottom. *Locations with traffic which may contribute to readings.

Ambien: Location	Date	Size	Duration (hrs.:mins.)	Average (mg/m^3)	Maximum (mg/m^3)	Minimum (mg/m^3)
Woodlands (villa)	14/01/10	PM4	07:15	0.07	0.029	0.003
Salem Clinic	22/01/10	PM10	18:34	0.042	0.514	0.008
	23/01/10	PM10	18:00	0.041	1.259	0.016
	24-25/01/10	PM10	40:46	0.027	0.472	0.002
	26-27/01/10	PM10	39:37	0.019	1.542	0.007
	28/01/10	PM10	16:42	0.011	0.439	0.004
Salem Zone A-B checkpoint*	28/01/10	PM10	05:29	0.061	0.489	0.010
St Augustine's School, Woodlands	29/01/10	PM10	04:49	0.036	0.871	0.009
Personal: Task	**Date**	**Size**	**Duration (hrs.:mins.)**	**Average (mg/m^3)**	**Maximum (mg/m^3)**	**Minimum (mg/m^3)**
Ash hosing	24/01/10	PM10	00:32	0.024	0.039	0.019
Policeman at checkpoint*	28/01/10	PM10	04:33	0.023	0.277	0.013

The highest exposure on average was at the Salem zone checkpoint. This was not recorded during an ash fall event, so the level reflects ash re-suspended from the road surface, possibly coupled with particulate from car exhausts. Away from the Salem checkpoint, the monitors were set at least 12 m from roadsides. Two other high exposures were recorded at Salem clinic and during ash-fall events (on January 23rd and the 26-27th). Here the maximum levels reached 1.5 mg/m^3, which is still much lower than the maximum of 10.8 mg/m^3experienced at the Little Bay roadside.

6.4.4 Observations of Dust Hazard Management

The ethnographic study had two key foci: i) what dust hazard information was clearly made available in the quarries and ii) what dust suppression (exposure minimizing) behaviours were adopted by the workers, both on a site-wide scale and on an individual one. Examples of these practices are given in table 6.1 in the introduction to this chapter.

Information displayed at quarries

Attention was paid to any notices displayed at the site detailing dust hazard or referring to protective respiratory equipment. In New Zealand, both major companies (Winstone Aggregates and Holcim) displayed dust hazard notices which are shown in Figure 6.15. They are very different in their approach: one notice reminds workers of the three main methods of dust control (with a focus on environmental management rather than health protection), whilst the other lists the company policy from the perspective of corporate responsibility, including that all sites must have a dust management plan (examples given in Appendix III), and that personal and site monitoring, as well as lung function testing, are conducted. Both companies also conduct annual spirometry tests at all of their sites.

Figure 6.15 On-site signage of dust hazard in New Zealand quarries.

At the LAVA pumice quarry on Yali, signage was displayed in the form of a poster (Figure 6.16) and, although it did not refer directly to dust hazard, a mask (carried in the hand rather than fitted over the nose and mouth) is illustrated as part of broader personal protective equipment (PPE) practices.

Figure 6.16 On-site signage of PPE including a mask (held rather than worn) at LAVA pumice quarry, Yali.

Additional signage displayed at the jetty and entrance to the quarry cited mandatory PPE, but did not illustrate methods of respiratory protection (Figure 6.17). However, respiratory protection was mandatory when entering the tunnels where material is transported (it comes through holes in the tunnel roof and falls onto the moving belt; Figure 6.18).

Figure 6.17 On-site signage of mandatory PPE at jetty and entrance to LAVA pumice quarry, Yali.

Figure 6.18 Notice to wear respiratory protection at entrance to tunnel in LAVA pumice quarry, Yali.

In contrast, no signage related to PPE was displayed at the Aegean Perlite quarry on Yali. There was also no signage at any of the sites in Montserrat.

Dust suppression: quarry-wide

One key method of dust suppression (as shown on the poster in Figure 6.15) is the use of water which prevents the re-suspension of dust by vehicles or wind. In the quarries in New Zealand it was common for a water-cart to spray all of the quarry roads (Figure 6.19). This was repeated as often as necessary (more frequently if the weather was very hot and dry) in order to keep the ground damp. A crude version of this was observed in Montserrat at one site, where a hose pipe was used to damp down the road from the stockpiled site, but it was far less effective, as shown in Figure 6.20.

Figure 6.19 A water-cart spraying water to prevent the dust from the road from becoming re-suspended at Puketutu island quarry, New Zealand.

Figure 6.20 Spraying water with a hose to minimise the dust from the road from becoming re-suspended at Little Bay, Montserrat. Note the worker is wearing his respiratory protection on his chin.

Dust suppression: individual

Few individual mitigation measures were observed at the quarries. Exceptions occurred during quality-control testing at the Bombay (New Zeland) and LAVA (Yali) quarries, as well as for one day at Little Bay on Montserrat. The quality-control testing involving hand sieving of screened material to ensure processor screens were yielding accurate results. High-efficiency type with a valve respirator, suitable for respirable dust hazard (FFP3), were worn by those conducting the testing, a materials scientist at Bombay and a foreman at Yali. Otherwise on Yali, workers performing tasks which exposed them to dust did not wear RPE (Figure 6.21).

Figure 6.21 A worker at LAVA pumice quarry climbs to an upper platform on the processor to shovel a mound of dust from it whilst stood in a visible dust cloud. He was not wearing any respiratory protection.

At Little Bay the only instance where workers were observed to be wearing masks was on 23/01/10 at Eddie's trucking holding site, when material was removed from the site and dumped on a container ship. This resulted in a large movement of trucks along the dirt road from Eddie's to Little Bay (see Figure 6.4) and accompanying re-suspension of dust (as shown in Figure 6.5 and 6.20). Masks were also handed out to staff following the arrival of a family member of the company's owner (Figure 6.22 and 6.23); it is not clear whether the masks were distributed owing to the family member's own job (in the health protection department) and awareness, or the fact they knew the field campaign involved dust monitoring and health. On the same day, the remaining workers felt they would be sufficiently protected by pulling their t-shirts over their faces (Figure 6.24).

Similarly, at the neighbouring block where the block-making machine sometimes got quite dusty, workers either pulled up their t-shirts or tied a bandana across their mouths and noses.

Figure 6.22 Two young quarry workers outside Eddie's trucking office in Little Bay wearing their masks. The man on the left was a visitor making some enquiries.

Figure 6.23 A truck driver wears his mask whilst taking material from Eddie's holding site to the jetty. He has his cab windows open as the air conditioning does not work.

At all the quarries, truck cabs and other work vehicles were fitted with air conditioning that contained filters to minimise the entrance of pollutants into the cabs. In New Zealand and Greece, the air conditioning was well-maintained and so workers rarely opened their windows unless they needed to shout brief instructions. At Little Bay however, the air conditioning often did not work and so drivers commonly left their windows open (Figure 6.23).

Figure 6.24 A quarry worker covering his mouth and nose with his t-shirt.

6.5 Discussion

This chapter has explored the exposure to, and management of, dust hazard in volcanic quarries. The results are evaluated here in the framework of the original hypotheses outlined in section 6.1 and the challenges of representative exposure monitoring are discussed.

6.5.1 Appraisal of hypotheses

1) The ambient exposure to quarry dusts differs depending upon the type of deposit being quarried and the location within the quarry.

The ambient exposure at the quarries varied, increasing in particular when the quarry was busy (due to vehicular re-suspension of dust) or dry and windy (aeolian re-suspension). However, the levels were generally within permissible limits. On the occasion that the limits were breached, the extreme values continued only for minutes.

Table 6.6 shows the PM10 levels at the quarries extracting material from mafic lave flows, intermediate ash and felsic pumice. The Sioutas cascade impactor filters revealed that

there can be large differences in the deposition of the ≤2.5µm fraction within a relatively small area. For example, the production rate of the processor at Yali was fairly constant during the field campaign, yet the air quality at three locations (the processor, the processor control tower (outside, above the processor) and the tunnel belt taking material to the processor) varied substantially (0.07-0.74 mg/m^3 8-hr TWA PM10) based on the accumulated mass on the filters. The measurements correlated well with those collected in tandem with the DustTrak. In Little Bay there was a large difference between a quiet day (where little material was moved) and a busy day when they entire remaining stockpiles were sold and transported onto a ferry (0.05-1.44 mg/m^3 8-hr TWA PM10).

The observations are based on surveys taken at a particular location on a given day and as such cannot be representative of average, year-round conditions. They are a "snapshot" of conditions for a particular set of variable parameters, notably weather patterns, economic factors and production rates (both how much material is being processed and the frequency of transportation). A complete assessment of exposure will thus require a long-term, holistic approach for monitoring the parameters at different times throughout the year.

2) *The personal dust exposure of quarry workers differs depending on their particular role within the operation.*

Quarry workers typically have a specific task which they repeat throughout their shift, with those in vehicles usually in an enclosed cab and those with varying roles (foremen, maintenance workers) usually on foot in different parts of the quarry. There was little difference in exposure levels for those working 'on foot' (0.035-0.325 µg/m^3 8-hr TWA) compared to those in cabs (0.015-0.367 µg/m^3 8-hr TWA). All the levels of exposure, however, were within permissible limits. The processor was the dustiest area in many quarries and so workers involved in maintenance are most likely to be at risk here. The risk is difficult to quantify, because prolonged activity at processors usually only occurs if a part requires repair. In such instances the processor is shut off to allow the repair to be completed and therefore the generation of dust is minimised.

The majority of mafic quarries wet screen their material as part of the processing because it can help with both crushing and effective screening (too many fines clog up the

sieve-like screens), as well as reducing dust emissions. Wet processing was not conducted in the felsic quarries of Yali for several reasons. The pumice being extracted is very soft and therefore does not require much physical stress to break it apart, so there is no crushing, only screening. Pumice also has a low density, so that the screens are not regularly cleaned with water. In the perlite quarry, rock is broken by a single crusher (as opposed about three crushers in the mafic quarries visited). However perlite is highly water-absorbent (880-900 kg/m^3 (Sinclair, 2012)) due to its hollow cavities (as shown in SEM images in Chapter 4), even after expansion (Torres & García-Ruiz, 2009). The perlite quarry, therefore, could not allow water to come into contact with the perlite and it was stored in a large plastic hangar ahead of export (shown in Figure 6.25).

Figure 6.25 The perlite stockpile hangar on Yali which prevents raw perlite from exposure to rainfall.

In New Zealand and Greece personal monitoring on drivers was conducted in vehicles with the cab windows closed so that the drivers could take full advantage of the air conditioning; in Montserrat air conditioning did not operate so workers typically had their windows rolled down (as shown in Figure 6.24). This difference may lead to the Montserratian workers being exposed to higher levels of dust as a result of re-suspension. A study on vehicles on quarry haul roads revealed that there was little difference in

exposure regardless of whether cab windows were closed or not (Thompson & Visser, 2001), which raises questions regarding the efficacy of air conditioning filters at separating out fine dust. Thompson and Visser's (2001) data are presented in Figure 6.26 and show a similar pattern of increased exposure resulting from passing vehicles as seen at the test quarries studied here (Figure 6.11).

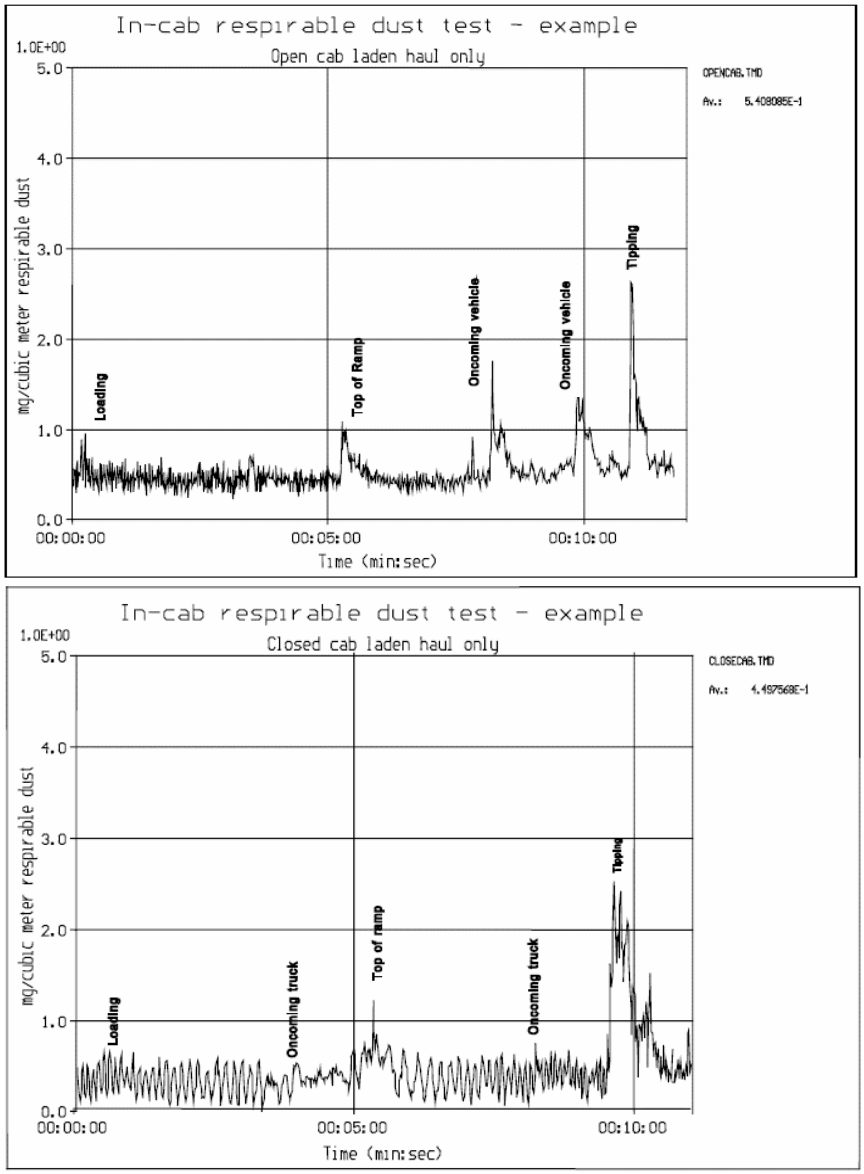

Figure 6.26 The level of PM4 mg/m3 in an open cab (top graph) and a closed cab (bottom graph) travelling over the same stretch of road within a quarry (Thompson & Visser, 2001).

The shift patterns of the workers in Greece and on Montserrat broadly follow an 8-hour, 5 day week. In New Zealand, however, some shifts were as long as 12 hours and therefore occupational limits may not be appropriate, despite meeting legal obligations. The lowest overall exposures were experienced at Hunua quarry, which, as the non-volcanic comparison, has the highest level of crystalline silica and a processor which is

enclosed in a shed and controlled via computer from a separate office. Informal conversations with quarry managers at Hunua, revealed that these measures were implemented because of the known crystalline silica content of the material and the size of the quarry (Hunua is the largest quarry in New Zealand), indicating that successful hazard management can be implemented where considered necessary.

On Montserrat, ambient monitoring was also undertaken in residential areas during episodes of ash venting from the Soufrière Hills volcano. Compared to some events in recent years, the levels of exposure were very low. Searl et al (2002) devised exposure limits specifically for those exposed to volcanic ash on Montserrat and determined that a PM10 level of <50 $\mu g/m^3$ (one hour average) as "low" and requiring no action, whereas levels of >50 $\mu g/m^3$ (one hour average) required actions such as use of masks (Searl *et al.*, 2002). The PM4 (respirable fraction) data collected during their 1996-1997 field campaign were far higher than are described here (e.g. average of 0.07 mg/m^3 over a 7 hour period in Woodlands), reflecting a more elevated level of volcanic activity and the production of ash by the collapse of lava domes, as well as by episodes of ash venting.

Hincks et al., (2006) determined the daily mean personal exposure for PM10 from a probability distribution (based on real sampling), the parameters of which are controlled by occupation, ground deposit depth and daily weather conditions. They focussed on western Montserrat (Foggarty, Woodlands, Salem, Cork Hill) and determined that a policeman working on a dry day would be exposed to a mean level of PM10 of 0.325 mg/m^3 and 0.122 mg/m^3 in minor (<1cm ground depth) and negligible (<1mm ash depth) levels of ash (Hincks *et al.*, 2006).

Similar measurements for this study monitored the PM10 exposure of a policeman (with the Sidepak personal monitor) working on a dry day at the Salem checkpoint between zones A and B, in a minor, but non-uniform, level of ash (<1cm; Figure 6.27). A Dustrak was also set up on the roadside near the checkpoint. The Sidepak and the Dustrak recorded respective average levels of 0.023 mg/m^3 and 0.061 mg/m^3. The levels are about an order-of-magnitude smaller than those expected from the model by Hincks et al., (2006) for ash depth of <1cm, although they are similar to those expected from only a negligible ash cover. The values from Hincks et al., (2006) refer to expected mean levels of ash exposure, whereas the new field data reflect actual values during one day. Large

variations about the mean may explain the discrepancy in expected and measured values. Another possibility is that the relation between ash in the air and on the ground changes with the size-distribution of the ash, which in turn may be affected by the proportions of ash produced by the collapse of lava domes and of ash venting. The first explanation suggests that the exposure values from the model of Hincks et al., (2006) are associated with large uncertainties, whereas the second suggests that the model can only be applied to the same type of ash-fall distribution as assumed in its development.

Figure 6.27 Policemen checking permits on a road partially coated with ash.

Cowie et al., (2002) conducted a health survey on 421 Montserratians occupationally exposed to volcanic ash. The study was undertaken after less than 5 years' exposure and included 84 participants (2% of the total) who worked in the construction industry, although not necessarily in quarrying. A slight reduction in average lung function was found amongst both the gardeners and the road workers, however, there were no radiological signs of silicosis (Cowie *et al.*, 2002). Two similar studies have been conducted

also upon children in Montserrat, a demographic considered more exposed owing to their short stature (dust levels are higher nearer the ground) and their propensity for outdoor play. One study was conducted in 1998 and raised some concerns regarding adverse effects upon respiratory health (i.e. asthma) and longer-term risk (Forbes *et al.*, 2003). The results however were not confirmed by a follow-up study in 2007 (Baxter, 2012).

A key issue with quarrying near an active volcano is that workers are exposed dually to volcanic particulate, from quarrying and eruptions. During ash fall their exposure will be greater therefore than that measured as part of their quarrying duties, especially if they are also responsible at home for ash clearance from their property. Whilst the cumulative exposure based on data presented here would still be quite low, the eruptive component was derived from ash venting, which is known to produce lower concentrations of airborne material than explosive eruptions or the collapse of lava domes. The "snapshot" presented here should thus be considered conservative, and for a complete evaluation further investigation is warranted over a longer time interval. Finally, several of the truck drivers at Eddie's also worked shifts as haulage for the shops on the island when goods arrived by ship. This may also contribute to their exposure if there is a lot of ash on the road surfaces.

3) *Mitigation and management of dust as a hazard differs amongst quarries on both a corporate (management) and individual (worker) scale.*

Legislative controls exist in the locations studied: they are quite specific in Greece and New Zealand but less clear in Montserrat. In fact it was not possible to obtain any information from a legislative stand-point with regard to occupational health and safety regarding quarry dust exposure on Montserrat. In some locations (notably New Zealand and Greece) a hard hat and boots were mandatory PPE but a dust mask was considered optional (although employers in all locations employers had FFP3 dust masks for their employees to use). Mandatory health and safety practices were often communicated through the use of posters and safety notices which were displayed in New Zealand and Greece but not in Montserrat.

The risk communication was quite formally presented in New Zealand and Greece through training, annual health monitoring and pamphlets and posters. In Montserrat the

quarry managers were not aware of any regulations regarding exposure levels and received no formal training or communication regarding use of the dust masks. Quarries in New Zealand and Montserrat made efforts to minimise dust exposure through the use of water to dampen down roads which were dusty. This was quite effective in New Zealand where a water cart was employed (see figure 6.11) but much less so in Montserrat where a hose was used. No such dust-control measures were observed at Yali, which had the higher levels of PM10 for both ambient and personal exposure than New Zealand and many of the Montserrat surveys.

Exposure limits are based on an 8-hr TWA average and the workers in New Zealand have such limits recommended in relation to their occupational exposure; their shift patterns, however, do not reflect an 8-hr working day but are far longer. The 8hr-TWA limits are based upon a pattern where the worker works for 8 hours then has 16 hours away from the quarry in less dusty air during which his or her lungs have an opportunity to clear dust before being re-exposed the following day. The 8-hr TWA may not be suitable, for workers who are regularly exposed to dust in excess of 8 hours, and additional guidelines need to be established, that better reflect actual working patterns.

The Winstone Aggregate quarries in New Zealand also have specific dust management plans which give both general and site-specific information. For example, at Flat Top there are suggestions including: minimising sizes of stockpiles, wearing respiratory protective equipment (RPE) around the processor if the material is dry (if it has been raining the material may be wet and not create as much dust), using minimum blast force (in explosions), reduced speed of vehicles and without downward facing exhausts (to prevent dust re-suspension). As part of local council legislation, specific to Flat Top quarry, there is a requirement for continuous monitoring of dust and water cart use as follows:

Continuous monitoring and recording of visible dust emissions, wind strength, wind direction and rainfall required as a condition of the Discharge to Air consent 9711836. Recording of frequency of water cart use, volume of water applied with the water cart and the volume of water used for dust suppression other than water cart use as per conditions of Discharge to Air consent 9711836 (Winstone Aggregates, 2009) .

The document states that the stockpile areas (see Figure 6.3) are 500m from the nearest residential dwelling in any direction and sheltered on three sides (exposed only to the north) so it is perceived that "*dust emissions are not likely to blow towards the road or neighbouring dwellings to the west and east*". As mentioned in the literature review and ethnographic study parts of this chapter, the dust that enters the lungs is too fine to be visible to the naked eye, so recording 'visible' dust may not be a helpful parameter in dust control. It is important to note, however that at all the quarries run by Holcim and Winstones, the workers receive an annual health check which includes lung function testing (spirometry) and therefore any emerging respiratory issues should be detected.

Although suitable dust masks (FFP3 type, with a filter) were available at all quarry locations they were worn only irregularly. At the LAVA quarry on Yali, masks were observed in use on just one occasion, when a foreman was sieving processed material as part of quality-control measures; however, another worker shovelling fines off the processor and surrounded by a dust cloud did not wear a mask. The quarry manager explained that although all workers had been issued with masks they typically did not wear them because they found them "hot and uncomfortable". Individual compliance with voluntary RPE is likely to result from increased risk awareness. This is a complicated issue which requires in-depth study and appreciation of various local social and political forces; a pilot study was carried out here (Appendix IV) suggest that workers judge whether to wear a mask based upon how much dust they see. This echoes previous questionnaire-based findings among Australian quarry workers, who also tended to wear masks when they saw that conditions were dusty (Hedges *et al.*, 2008). The notion that respirable dust can be "seen" is misleading for two reasons. First, respirable (PM4) dust cannot be seen by the naked eye. Second, the presence of coarser (potentially visible) dust does not correlate with the incidence of respirable dusts, as was shown here by the lack of relationship between different size fractions deposited on filters (Table 6.7 and Figure 6.13).

6.6 Conclusion

Without permanent monitoring stations, it is very difficult to build a clear picture of exposure to PM10 at quarries that accurately reflects the relative contributions of the factors controlling levels of emission. Whilst the quarrying process is broadly the same at each quarry, the details regarding the regularity of blasting, the number and types of vehicles employed, the use of dust suppression measures and the resulting levels of exposure are all highly variable. Similarly, the range of deposits from solid lava flows to friable ash deposits, leads to considerable variation in the physicochemical characteristics of the dust (Chapter 4).

The blasting which occurred at the basaltic and greywacke quarries was found on occasion to create elevated levels of PM10 but none exceeded permissible levels. These emissions are likely to be comprised of drilled fines (created prior to blasting), the smoke particles from the explosives themselves and fines created as a result of the rock breaking up during the blast. The level of emissions could thus be reduced by removing the drilled fines prior to blasting.

At quarries on Montserrat and New Zealand some workers conducted shifts longer than 8 hours and it is possible therefore that the 8-hr TWA OELs may over-estimate safe levels during such shifts. Although the volcanic deposits studied here appear of lesser health concern than other deposits (e.g. greywacke, sandstone), further scrutiny of the usefulness of the 8hr TWA system may be warranted in areas where shifts regularly exceed 8 hours. Furthermore, at quarries where workers are exposed to higher levels of particulate (e.g. on Montserrat) through combined exposure from quarrying and volcanic eruptions, a more effective dust control strategy could be implemented, such as a water cart instead of a hose. Air conditioning should also be maintained with appropriate filters to prevent workers driving with their cab windows open as this may help to reduce exposure.

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Chapter 7 – Physicochemical controls on the reactivity and potential toxicity of quarried volcanic material: A discussion of health-pertinent parameters

7.1 Introduction

The airborne health hazard of dusts from the quarrying of volcanic deposits is broadly governed by two factors: i) the physicochemical characteristics of the dust, including surface reactivity ii) the workers' exposure levels and durations.

A holistic assessment should ultimately combine all of these parameters and determine which are related and how they influence each other. This can be challenging to achieve with a mixed natural dust because it is difficult to control all of the highly variable parameters to the exclusion of the one being investigated. Furthermore, natural dust does not behave in the same way as laboratory standards, so it can be difficult to determine whether trends between parameters observed under laboratory conditions may hold true in nature. The lack of clear thresholds (significant, health-relevant values) for both physicochemical and toxicological parameters heightens the challenge associated with determining the potential hazard associated with airborne volcanic quarry dust; put simply, for any of the parameters: how much is too much? This challenge highlights the need for the use of both laboratory standards and analogous samples, within the hazard assessment, as these can help to provide some context to the results from this study.

The physicochemical characteristics of mineral dust include the particles' elemental composition, size, surface area, morphology and the presence of minerals of health concern, such as crystalline silica; these were characterised in Chapter 4. The resultant surface reactivity and potential toxicity, as determined through measurements of hydroxyl radical production and haemolysis, were explored in Chapter 5. This chapter aims to synthesise the findings across these parameters and ascertain, as far as possible, the likely physicochemical controls on particle reactivity and potential toxicity. Some comparison is also made with the workers' exposure to airborne dust concentrations (as investigated in Chapter 6).

7.2 Physicochemical Controls on Surface Reactivity

Surface reactivity was determined by investigating the iron-catalysed production of hydroxyl radicals through the Fenton reaction. In general, the volcanic quarry dusts did not generate substantial radicals and less than volcanic ash. The potential controls on these findings are discussed here.

7.2.1 The influence of surface area on particle reactivity

Surface area is thought to be a key control for particle toxicity (Donaldson *et al.*, 2007, Duffin *et al.*, 2002) (Chapter 2, Section 2.6.6). Assuming all other parameters are equal, the surface reactivity of dust particles ought to increase commensurately with their surface area (Fubini & Otero-Areán, 1999). In a mixed natural mineral dust, it is unlikely that all other parameters will be equal, especially in the comparison of dusts from different deposits (even if they are from a similar magma type or mode of emplacement); therefore, the influence of surface area on reactivity and potential toxicity ought to be determined on the basis of individual deposits.

The data on hydroxyl radical generation and iron release were expressed as a function of surface area in Chapter 5 Section 5.4.1 (i.e. $\mu mol/m^2$) precisely because surface area is likely to be a controlling factor in surface reactivity. In order to unravel the influence of surface area here, these data are now explored without normalisation for surface area.

Figure 7.1 shows the concentration of radicals produced (in µmol) after 30 minutes (Chapter 5, Table 5.2) versus their surface area (Chapter 4, Table 4.8) for the three magmatic groupings: A) mafic, B) intermediate and C) felsic. The non-volcanic comparators which were analysed in Chapter 5 are useful for comparing reactivity with volcanic quarry material, but are excluded from comparisons here as they represent two samples of raw material and finished product; the latter has undergone extensive surface modification (including a change in surface area) as a result of processing, and will therefore not yield useful comparison.

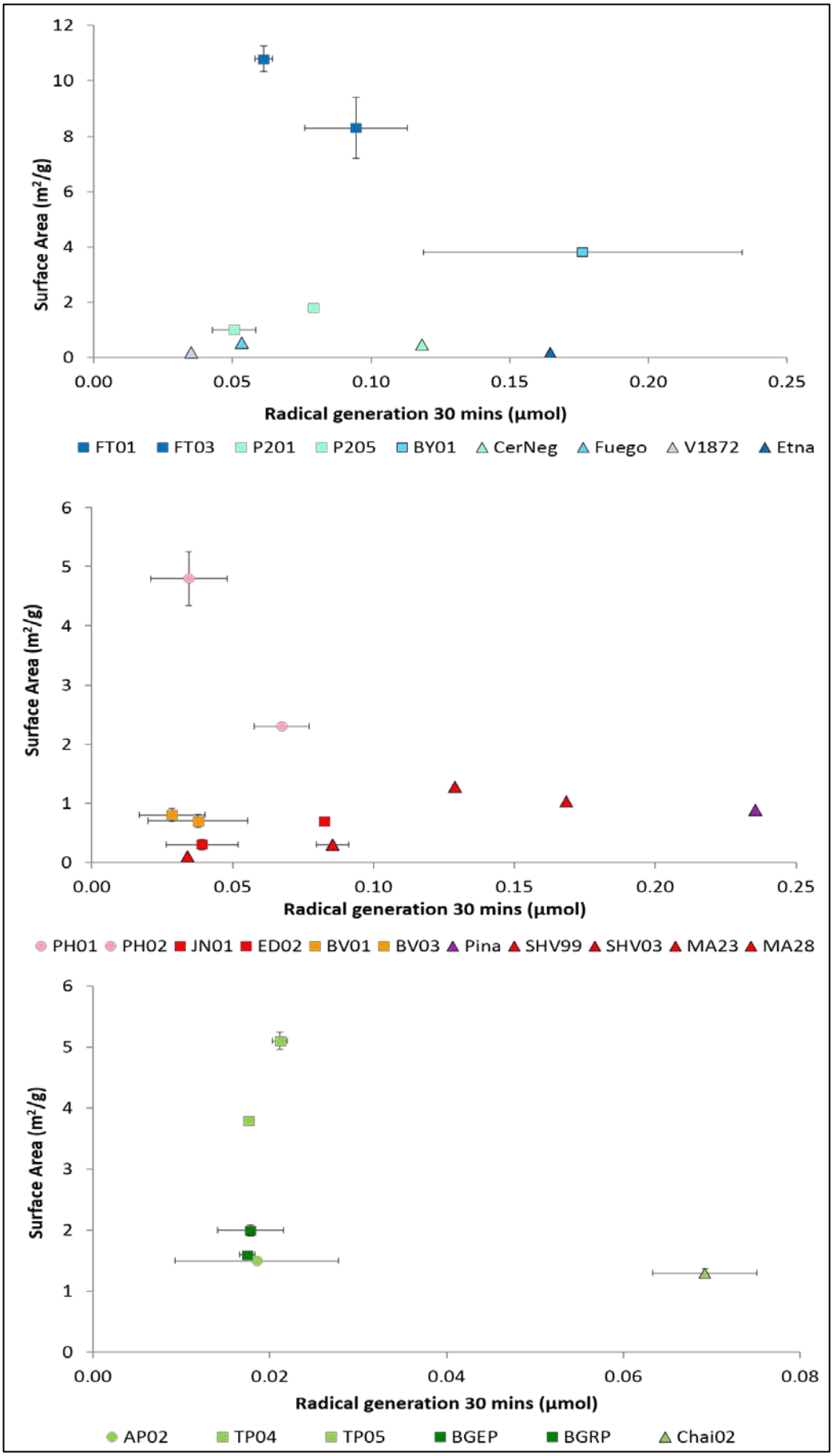

Figure 7.1 Hydroxyl radical generation (µmol after 30 mins) versus surface area (m^2/g) for <1mm dusts. Error shown is 1σ (N=3), note differences in scale.

No clear relationship is observed between surface area and radical production for any of the magmatic groupings. Samples from different deposits are likely to differ in their reactivity (potentially from differences in their iron content, discussed in 7.2.2), therefore results must be investigated on a quarry-by-quarry basis; however, there are few samples analysed from each quarry so any associations will be tentative. In Figure 7.1A the two samples from Puketutu (P201 and P205) show a positive relationship between radical generation and surface area, as do two samples from Trants (JN01 and ED02) in Figure 7.1B and two samples from Te Puke (TP04 and TP05) in 7.1C. Two data points per quarry are too few to infer a trend, however. If the assumption is made that these deposits are fairly uniform in their iron release, then additional samples from the same quarry may also exhibit a positive relationship between surface area and associated reactivity.

Some quarries show a negative relationship between surface area and radical generation, notably the two from Flat Top (FT01 and FT03, Figure 7.1A) and from Little Bay (PH01 and PH02, Figure 7.1B). Again, with only two data points a trend cannot be inferred, however, a lack of correlation does not indicate that surface area does not influence surface reactivity. There may be several reasons why a lack of positive relationship might be observed; the deposit sampled may not be uniform in its bulk composition resulting in a variation of surface iron ions when dusts particles are generated, some samples may be more weathered than others (e.g. a sample taken from the stockpile versus a sample obtained from freshly extracted raw material), or other physicochemical parameters may also be contributing to reactivity which may mask the influence of surface area.

One potential reason for the lack of relationship between surface area and generation of hydroxyl radicals is a lack of relationship between the removable Fe^{2+} (required for $^{\bullet}OH$ generation) and surface area, for example, if surfaces are not uniform in their distribution of surface iron ions. Figure 7.2 shows the removable Fe^{2+} released by chelation after 7 days (Chapter 5, Table 5.2) against the surface area (Chapter 4, Table 4.8). A correlation between surface area and Fe^{2+} release may be expected for those samples that naturally contain iron-bearing minerals, notably the mafic (shown in blues) and intermediate (shown in pinks and oranges) ones.

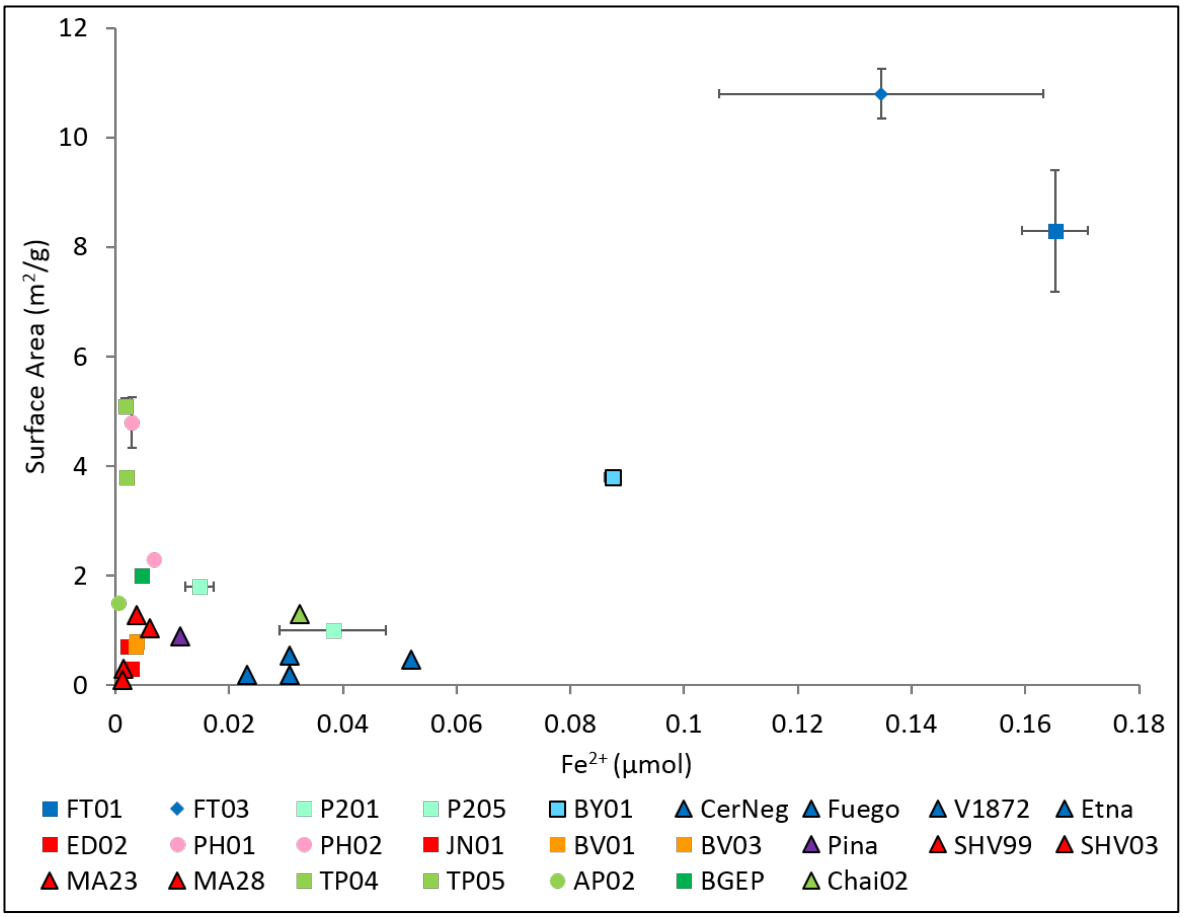

Figure 7.2 Release of Fe^{2+} after 7 days (in µmol) versus surface area (m^2/g) for dusts <1mm. Error shown for surface area on all quarried samples (<1mm) is to 1σ (N=3), for Fe^{2+} release on quarried mafic (FT, P2 and BY) and intermediate (ED, PH, JN, BV) samples the error is to 1σ (N=3).

Overall, there may be a broad association of samples with high Fe^{2+} release having a larger surface area, but there is no clear correlation. The two Flat Top samples have high iron release and surface areas in comparison to the other samples, which is in keeping with studies on volcanic ash which indicate a similar association for samples which release greater amounts of Fe^{2+}. This lack of a clear relationship may be due to some samples being weathered; for example, sample FT01 is from freshly drilled fines, and has a higher reactivity (but a lower surface area), than sample FT03 which was obtained from the stockpiles where it will have been exposed to water during processing and will have had longer environmental exposure in the stockpile. The lack of relationship between release of Fe^{2+} and the surface area of the particles may contribute to the lack of relationship between surface area and hydroxyl radical generation; however, other factors, such as the bulk content of the iron may also play a role and is discussed in Section 7.2.2.

Whilst the proportion of lung-pertinent material in a sample is an important physicochemical parameter (as only particles fine enough to penetrate the lung have the potential to cause toxicity), the grain size of dust has been shown to exert less influence on potential reactivity than a particle's surface area (Clouter *et al.*, 2001, Duffin *et al.*, 2002, Duffin *et al.*, 2007, Fubini & Otero-Areán, 1999). Here, no obvious correlation was observed between the proportion of <10μm material (Chapter 4, Tables 4.6 and 4.7) and the generation of hydroxyl radicals (shown in Appendix V). Although there can be a positive relationship between surface area and grain size, no clear relationship was observed for the samples in this study (Chapter 4, Figure 4.32), which is likely to contribute to the lack of positive relationship between grain size and hydroxyl radical generation.

7.2.2 The influence of bulk composition on particle reactivity

The production of hydroxyl radicals from particle surfaces is through the iron-catalysed Fenton reaction. In Chapter 5, the relationship between iron release (which should represent the iron available for reaction by Fenton chemistry) and hydroxyl radical generation has already been explored and a weak associated was noted (Chapter 5, Figure 5.6), indicating that, actually, iron-release is not the sole controlling factor. Whilst the bulk composition (as determined by XRF) does not provide an indication of the oxidation state of iron present on particle surfaces, it can be used to determine whether iron is present in the particles and, thereby, potentially on their surfaces and thus may correlate with hydroxyl radical generation.

Here, bulk iron content is explored as an indicator of $^{\bullet}OH$ production in Figure 7.3 A) for volcanic quarry dust and ash samples, and B) for quarry dust only. Overall there are discrete groupings by magma type for Fe_2O_3 content in keeping with magma composition i.e. mafic magmas contain more Fe-bearing minerals compared to intermediate ones and felsic magmas contain very little. Overall in A), there is no clear relationship between bulk Fe_2O_3 content and hydroxyl radical generation, due to the wide spread of radical generation by volcanic ash samples. In Figure 7.3B, where the quarry samples are plotted alone, there is also no clear relationship between bulk Fe_2O_3 content and the generation of hydroxyl radicals. This lack of correlation, between volcanic ash and quarry dust, is

likely to result from the differing surface functionalities; as described in Chapter 5, Section 5.5, where it is demonstrated that, particularly in the case of volcanic ash, radical generation is not controlled solely by the release of iron.

Due to the lack of correlation between bulk Fe_2O_3 content and hydroxyl radical generation, and the fact that Fe_2O_3 is unreactive on particle surfaces (Fubini *et al.*, 1995), a lack of correlation would also be expected for bulk Fe_2O_3 content and the release of Fe^{2+}. This is explored in Figure 7.4.

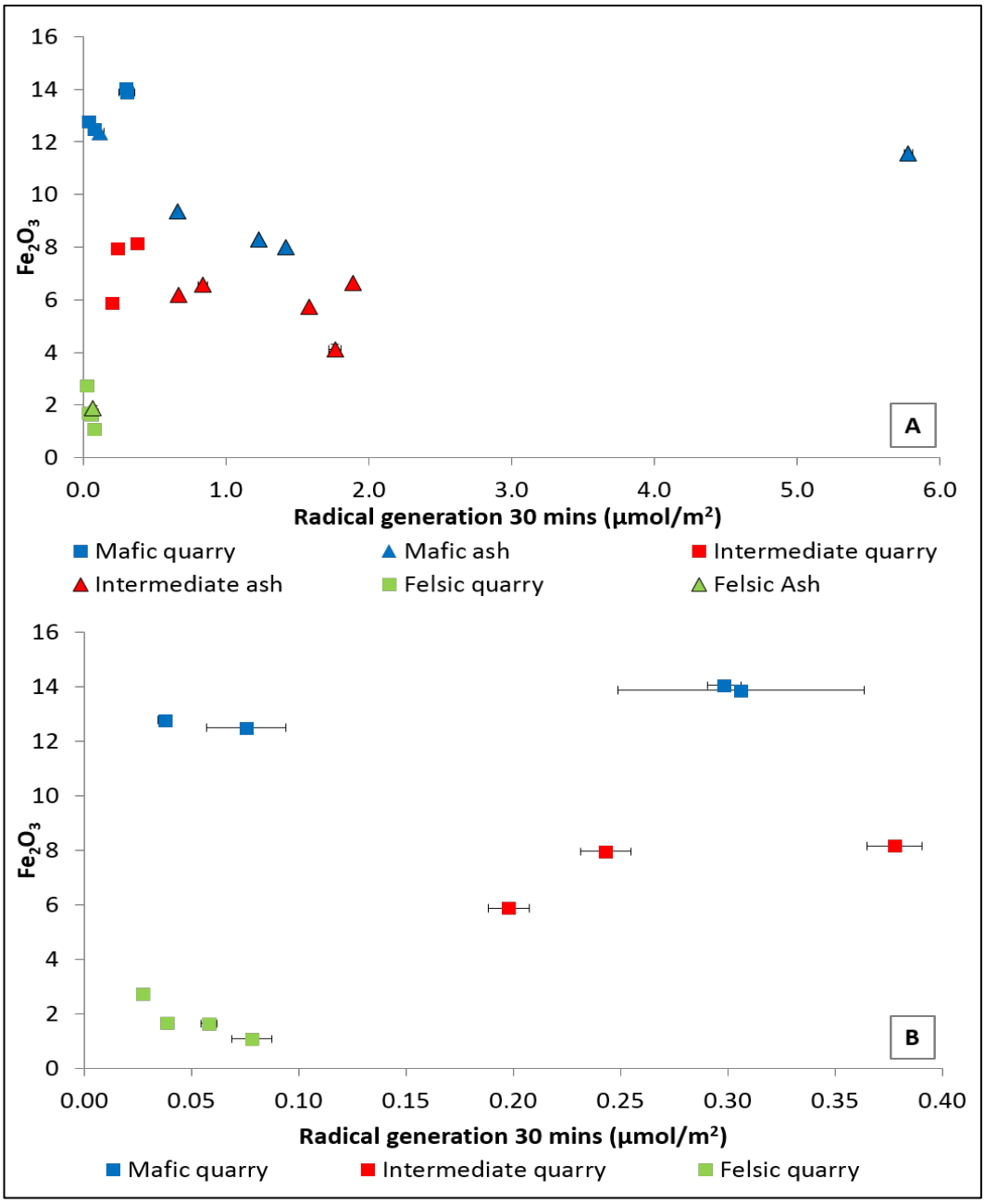

Figure 7.3 Hydroxyl radical generation after 30 mins (µmol/m^2) versus Fe_2O_3 (oxide wt.%) for A) volcanic quarry samples and ash, and B) volcanic quarry samples only (all samples <1mm). Error shown on radical data is 1σ (N=3).

Figure 7.4 shows the removable Fe^{2+} (required for $^{\bullet}OH$ generation) released after 7 days (Chapter 5, Table 5.2) against the Fe_2O_3 (Chapter 4, Table 4.7) for mafic (blues), intermediate (pinks and oranges) and felsic (green) samples of volcanic quarry dust and volcanic ash in A) and quarry dust only in B).

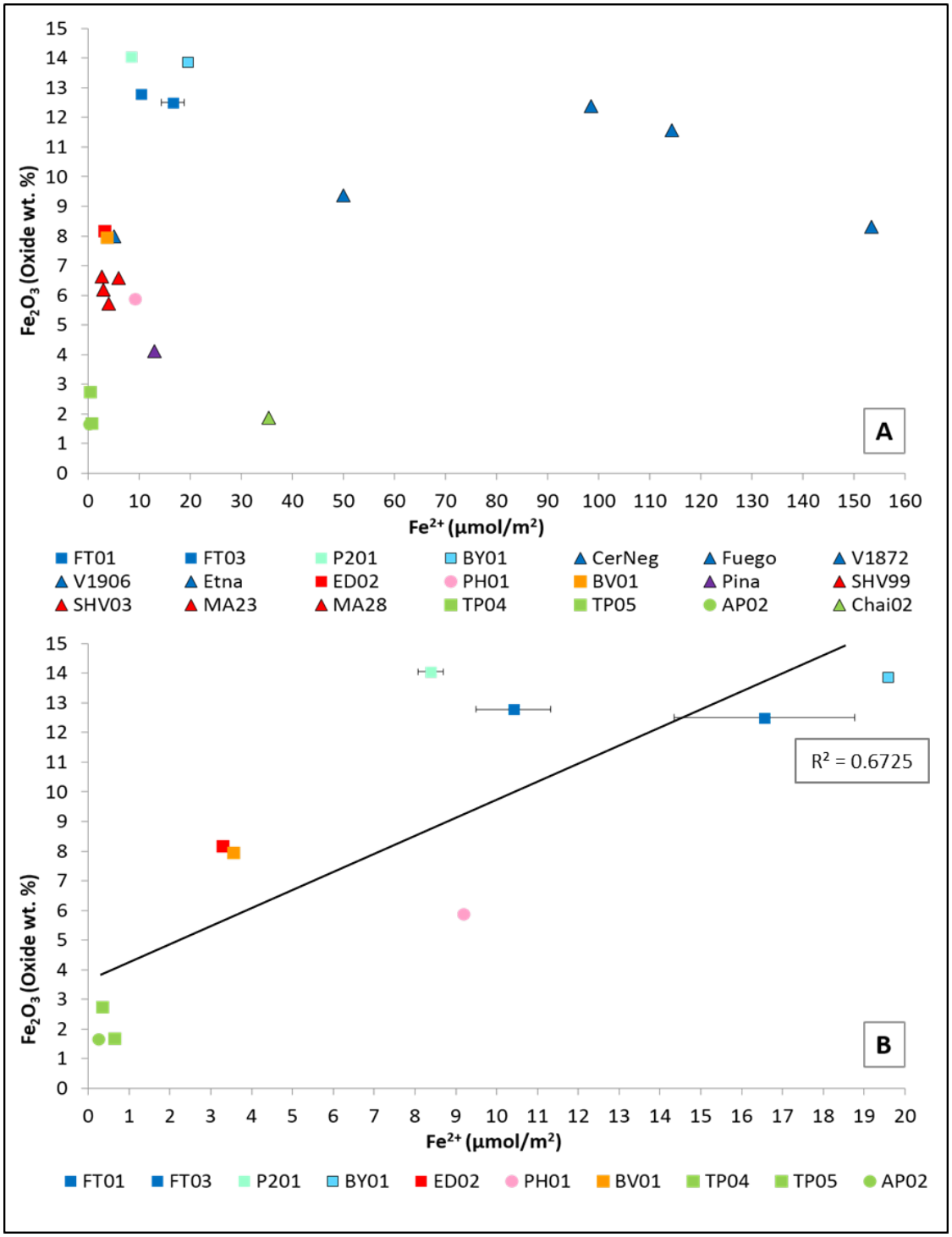

Figure 7.4 Release of Fe^{2+} (µmol/m^2) after 7 days versus Fe_2O_3 (oxide wt. %) for A) mafic (blues), intermediate (reds) and felsic (green) samples of volcanic quarry dust and volcanic ash, and B) quarried samples only (all samples <1mm). Error shown on Fe^{2+} data, for mafic quarry samples only is to 1σ (N=3). Note change in scale on x axis.

As expected, there is poor correlation for volcanic ash samples between the bulk Fe_2O_3 and release of Fe^{2+}, particularly for the mafic samples (Figure 7.4 A). For the quarried samples (Figure 7.4 B) there is broadly concomitant release of Fe^{2+} with bulk Fe_2O_3, with moderate linear regression (R^2=0.67) indicating a likely positive relationship. This suggests that for quarry dusts (conversely to ash), bulk iron content may be indicative of the propensity of the sample to release Fe^{2+}. There is, however, a wide variation in Fe^{2+} release exhibited by the intermediate and mafic samples, so this potential relationship would benefit from further study with a larger data set.

7.2.3 Implications

No clear relationship was observed between either surface area and the generation of hydroxyl radicals, or, between surface area and the release of divalent iron, although a potential weak correlation was observed for the latter in the case of mafic samples.

The volcanic ash samples in this suite have comparatively low surface areas and, whilst they are useful as a comparison of reactivity for the quarry samples, it is not feasible to compare them in the context of influence of surface reactivity as they are erupted from different sources and will probably have differences in associated surface reactivity. The exception to this is the set of four samples from the Soufriere Hills Volcano, two from dome collapses (data obtained from Horwell et al., (2003)) and two ash-venting episodes which occurred during the field season; these two ash-venting samples (MA23 and MA28) are less reactive than the dome-collapse samples (SHV99 and SHV03) and show variation in both surface area and surface reactivity, despite being erupted only 5 days apart. This variation highlights that active volcanoes are dynamic systems and therefore it can be problematic to attempt to infer trends between physicochemical parameters and reactivity.

Similarly, quarried volcanic deposits are unlikely to have been uniform when emplaced and may have undergone further post-depositional changes resulting from weathering and secondary mineralisation. This combination of factors (few samples coupled with potential combined influence from other parameters) makes it difficult to

state to what extent surface area might influence reactivity as demonstrated by the suite of quarried volcanic particulate in this study.

It would be useful to be able to use bulk composition as a potential determinant of likely radical generation in relation to the iron-catalysed Fenton reaction. For the quarried samples analysed here, this may be possible to a certain degree as there was some correlation observed between both bulk Fe_2O_3 and subsequent release of divalent iron and associated hydroxyl radical generation, which shows that bulk composition might be employed as an indicator of likely Fenton reactivity.

The ash samples, displayed a greater variation across both bulk Fe_2O_3 and release of Fe^{2+} in comparison to the quarry samples. As discussed in Chapter 5, the iron release and reactivity is significantly different ($p \leq 0.01$, Section 5.4.2) between volcanic ash and volcanic quarry dust of a similar magma type. This is substantiated here because it shows that, whilst the quarried mafic samples contained more wt.% Fe_2O_3, they released far less Fe^{2+} than the volcanic ash samples, which may be due to the quarry samples having oxidised surfaces as a result of weathering.

Contrary to the quarried samples, the volcanic ash showed a lack of relationship between bulk Fe_2O_3 and both the release of Fe^{2+} and the generation of hydroxyl radicals. This is in keeping with the findings of previous studies on mineral dusts and volcanic ash (Damby *et al.*, 2013, Fubini & Otero-Areán, 1999, Horwell *et al.*, 2007, Horwell *et al.*, 2003). Several factors are known to control iron release including: the crystalline structure of the particle, the surface area of the particle, the coordination of the Fe ions and their redox state (Elias *et al.*, 2002, Fubini & Mollo, 1995), which could explain why a clear relationship between bulk and surface iron, and radical generation is not observed for the ash samples. Furthermore, as outlined in Chapter 5, there was no clear relationship observed between iron release and hydroxyl radical generation, which is likely to result from: i) the fact that not all iron on the surface is available for free radical release, e.g. iron on particle surfaces in the form of Fe_2O_3 and Fe_3O_4 is inactive (Fubini *et al.*, 1995) and ii) an excess of iron can also lead to a reduction in reactivity (Elias *et al.*, 2002, Gulumian, 2005). Finally, the oxidation state of Fe itself can change following inhalation as the lung lining can both chelate (due to metal-binding proteins) and reduce (by interaction with ascorbate or superoxide ions) (Damby, 2012, Fubini & Otero-Areán, 1999). The relationship between iron on particle surfaces and resultant reactivity is,

therefore, complex and cannot always be clearly predicted by determining bulk iron content.

7.3 Physicochemical Controls on Haemolytic Activity

Haemolysis has been used in this study as a first order *in-vitro* toxicity test. Typically it is used in volcanic ash studies to indicate the likely biological toxicity of particulate in relation to crystalline silica. Crystalline silica is not the only mineral which is capable of provoking a positive haemolytic reaction; however, it is the only major mineral phase in volcanic ash which may be expected to generate haemolysis (Damby, 2012). Here, samples of volcanic quarry dust (<1mm and <10µm) which are both enriched and poor in crystalline silica were analysed (for reasons of comparability) along with a range of volcanic ash samples, non-volcanic quarry dusts and standards.

The two most likely physicochemical controls on haemolysis are: surface area and crystalline silica content (Damby *et al.*, 2013, Horwell *et al.*, 2013). As outlined in 7.2.2, surface area has a greater influence on exhibited surface reactivity (for both radical generation and haemolysis) than grain size; but, again, there was no observed relationship between the proportion of <10µm material (Chapter 4, Tables 4.6 and 4.7) and haemolysis (Chapter 5, Section 5.4.4), shown in Appendix V. As discussed previously, this is likely the result of a lack of correlation between grain size and surface area (Chapter 4, Figure 4.32).

As noted, crystalline silica content can be a driver of haemolysis, as its toxicity causes the cell membrane to rupture. In Chapter 5, some samples which are poor in crystalline silica exhibited haemolysis (potentially due to the presence of clays) however, the relationship between crystalline silica content and haemolysis has not yet been explored and therefore is investigated here.

7.3.1 The influence of surface area on haemolysis

As outlined in 7.2.1 if all other parameters are the same, there should be a positive relationship between particle induced haemolysis and surface area. However, with natural samples, natural variation is likely to play a role, even when comparing samples from the same deposit.

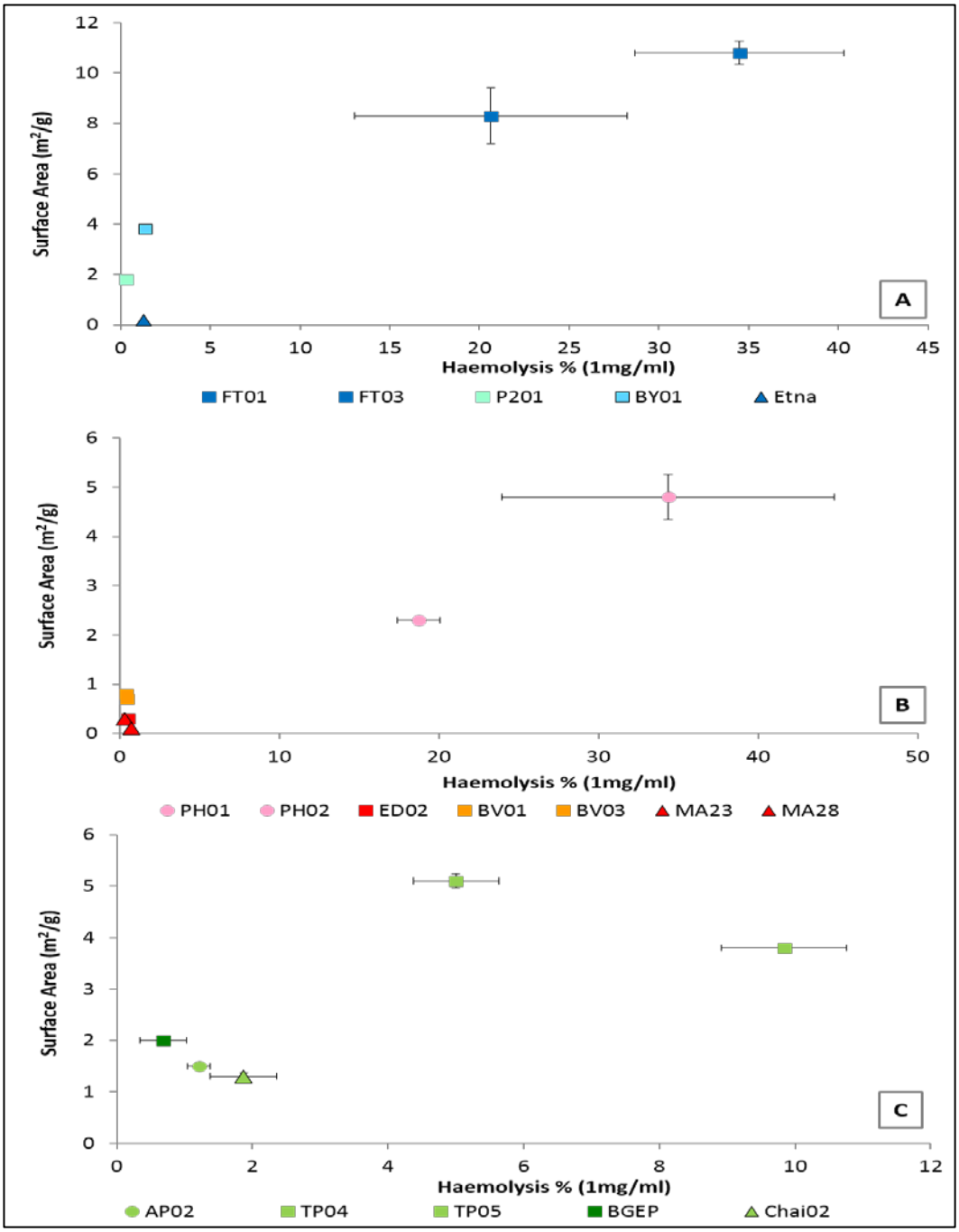

Figure 7.5 Surface area (m^2/g) versus haemolysis % (at the highest concentration of 1mg/ml) for volcanic quarry dust and volcanic ash, grouped by A) mafic magmas, B) intermediate magmas and C) felsic magmas (all samples <1mm). Error on surface area is to 1σ (N=3); error on haemolysis is standard error of the mean (σ/√N) (N=3). Note differences in scale.

Figure 7.5 shows the surface area versus the haemolysis % for volcanic quarry dust and volcanic ash, grouped by A) mafic magmas, B) intermediate magmas and C) felsic magmas. A and B appear to show a positive relationship between surface area and haemolysis, with those samples with elevated haemolysis (FT01 and FT03 on 7.3A, PH01 and PH02 on 7.3B) also having commensurately larger surface areas. There is no correlation for those samples which exhibited little haemolysis, despite having variable surface areas; this observation extends to the felsic samples (Figure 7.5 C) which exhibited low haemolysis and had low surface areas. Two felsic samples showed elevated haemolysis which does not appear to relate to surface area (TP04 and TP05) as the sample with more haemolysis had a slightly lower surface area. This is likely to be mainly due to processing as the more haemolytic sample is finished product (which may have freshened surfaces resulting from abrasion during screening) whilst the less haemolytic sample is raw material.

The large error bars on the haemolytic samples indicate how variable biological toxicity assays can be when analysing natural materials. This highlights the value of running laboratory standards alongside the samples to be investigated as they provide a useful comparative benchmark, however, it also shows the compounded challenge in attempting to isolate parameters of interest in order to try to determine their significance in influencing the overall toxicity of the particles tested. Surface area, therefore may exert some control on haemolysis but is not the sole controlling factor. This has also been found to be the case in haemolysis analyses of diatomaceous earth (Nattrass, In prep.).

7.3.2 The influence of crystalline silica content on haemolysis

Crystalline silica is a known human carcinogen and its potential toxicity has been assessed here by measuring its haemolytic activity. There is some debate as to whether quartz is a more toxic polymorph than cristobalite or vice-versa (Donaldson & Borm, 1998, Fubini *et al.*, 2001, Hemenway *et al.*, 1990), however, as both are listed as human carcinogens (IARC, 1997) the combined crystalline silica content is explored here. Some samples from intermediate and felsic magmas contained appreciable quantities of crystalline silica; however, a range of samples from the whole suite (across all magma types) were selected for the haemolysis assay, in order to better determine whether any haemolytic activity

observed was due to the presence of crystalline silica, or whether other factors may play a role.

Figure 7.6 shows the haemolysis in % plotted against the crystalline silica content of volcanic quarry dust samples A) mafic, B) intermediate, C) felsic, and D) non-volcanic quarry dust and the DQ12 standard. There is no trend to be observed among any of the volcanic quarry dust samples. Despite containing only 1wt. % crystalline silica, the mafic samples (Figure 7.6A) showed elevated haemolysis for samples from Flat Top quarry (FT01 and FT03) and no appreciable haemolysis for samples from Bombay and Puketutu quarries (BY and P2) which did not contain any crystalline silica. The intermediate quarries showed some haemolysis for samples from Little Bay quarry (PH01 and PH02) which contained 18 wt. % crystalline silica; however, samples from Trants and the Belham Valley also had elevated levels of crystalline silica at 14 and 9 wt. % respectively, but did not show any haemolysis. The felsic samples (Figure 7.4C) showed variability between both haemolysis and crystalline silica content and appear randomly distributed.

The non-volcanic quarry dusts (Figure 7.6D) might potentially show a positive trend between crystalline silica content and haemolysis, however, with so few data points, any inferences are of a potential pattern rather than a definitive relationship. The DQ12 samples are the most haemolytic, more so even than the two samples of sandstone (MSR and MSCr) which contain around 10 wt. % more crystalline silica than DQ12; this is broadly in keeping with a previous study by Clouter et al. (2001) which also compared two workplace samples of sandstone with a similar crystalline silica purity to DQ12 and found that the DQ12 had greater ability to cause prolonged inflammation. The sample of greywacke (HU04) contained less crystalline silica and commensurately elicited less haemolysis than the sandstone samples (MSR and MSCr) and positive controls in Figure 7.6D, despite having a greater surface area than the sandstone samples. This shows that several parameters are inter-related in their influence over particle toxicity in the haemolysis assay.

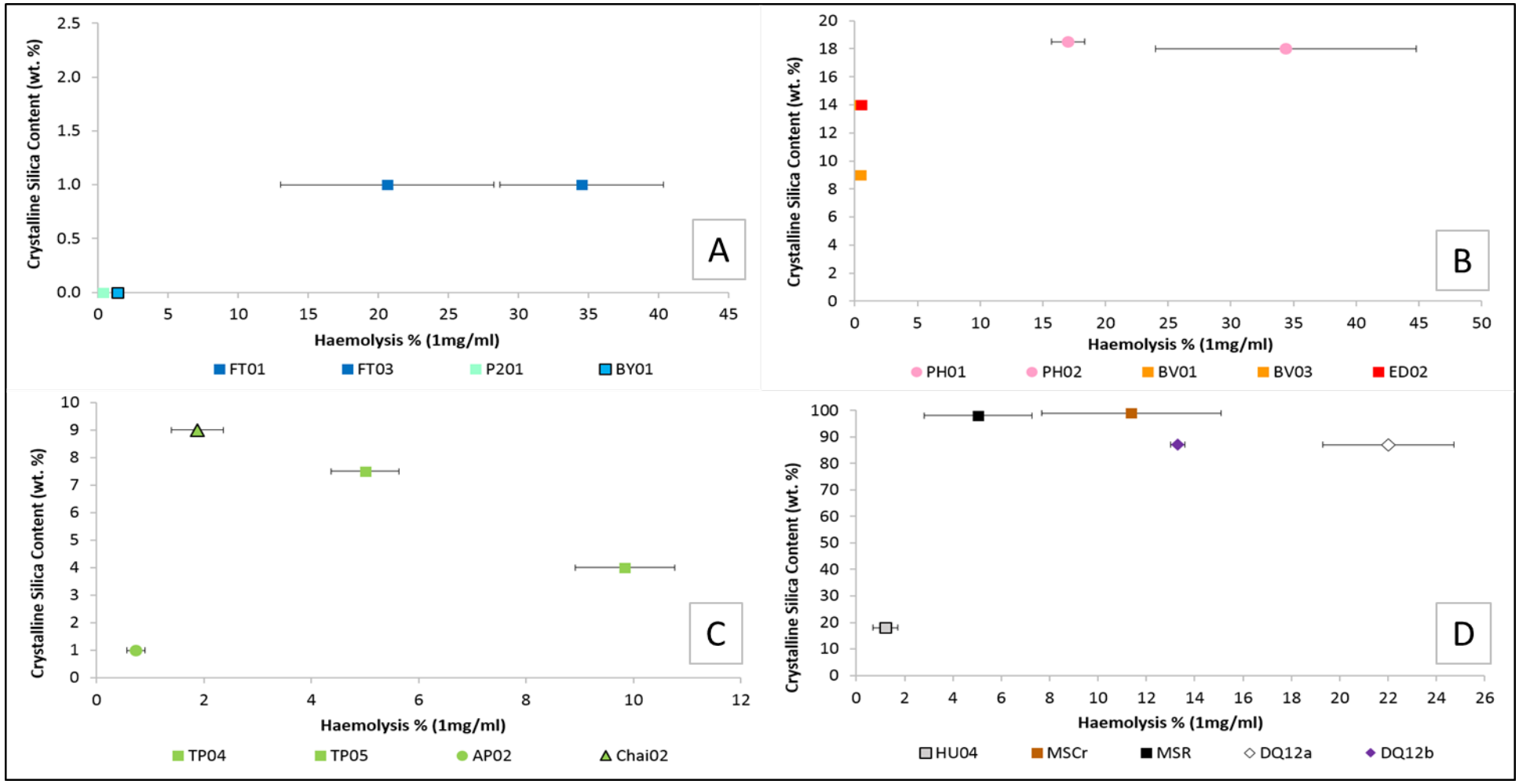

Figure 7.6 Crystalline silica content (wt. %) versus haemolysis % (1mg/ml), grouped by A) mafic magmas, B) intermediate magmas and C) felsic magmas (all samples <1mm). Error on haemolysis is standard error of the mean (σ/√N) (N=3). Note differences in scale.

Only the crystalline silica content and haemolysis assay were repeated on samples of the <10µm separated fraction. Here, it was found that for some samples, crystalline silica content was higher in the <10µm fraction as compared to the <1mm fraction (Chapter 5, Section 4.5.3), in keeping with a previous study of similar material by Horwell et al. (2003). The difference in haemolysis between the two fractions was not significant, which is also in keeping with other studies on volcanic ash (Damby, 2012) and diatomaceous earth (Nattrass, In prep.). This further supports the hypothesis that for the volcanic quarry samples in this study which exhibited elevated haemolysis, the cause of that haemolysis is not the crystalline silica content. Figure 7.7 shows the crystalline silica content versus the haemolysis for the separated <10µm fraction, which does not show a clear relationship. There is a large difference in the crystalline silica content of the mafic samples (FT01 and FT03 which contain 1wt. % crystalline silica) and the felsic samples TP04 (11wt. % crystalline silica); however, the variation in average haemolysis is very small, indeed allowing for error, there may be no difference in haemolysis at all. The intermediate sample PH02 also exhibited a similar level of haemolysis to the mafic and felsic samples but contained substantially more crystalline silica (~27 wt.%) whereas the other sample from the same quarry PH02 contained a comparable amount of crystalline silica (29 wt. %) but exhibited >10% more haemolysis. The use of a lung pertinent fraction, therefore, to make comparisons between single parameters and their influence, is just as complex as for the <1mm fraction sieved from the bulk.

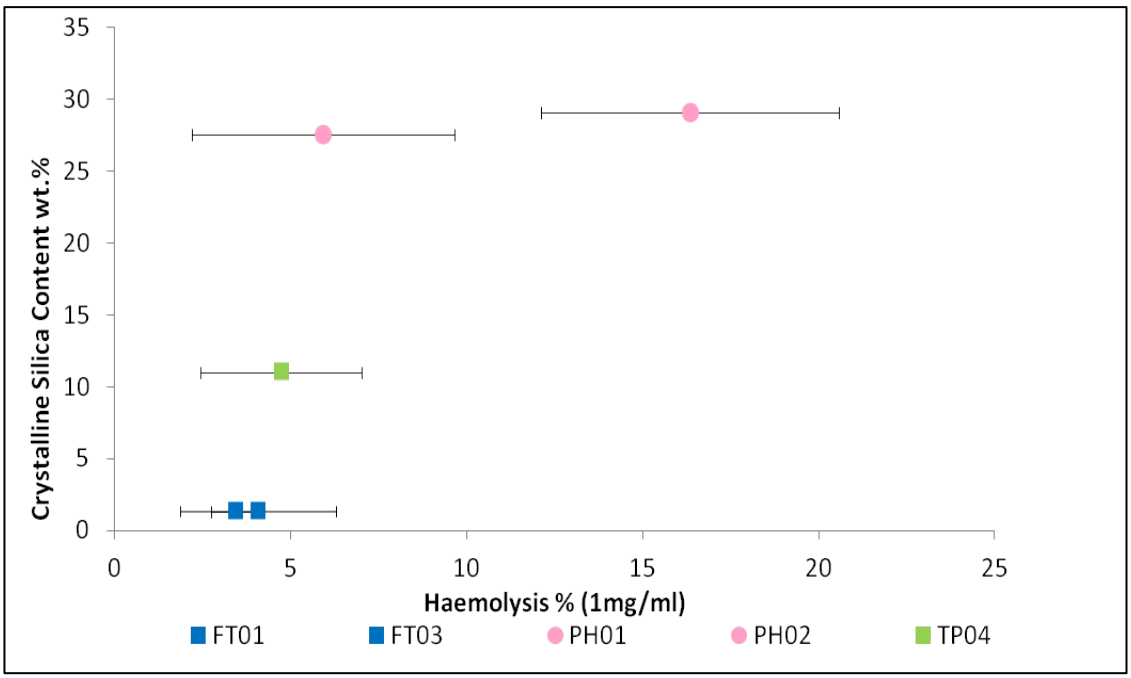

Figure 7.7 Crystalline silica content (wt. %) versus haemolysis % (at 1ml/mg) for the separated <10µm fraction. Error on haemolysis is standard error of the mean (σ/√N) (N=3).

Recent studies of volcanic ash indicate low toxicity of these samples for the haemolysis assay (Damby *et al.*, 2013, Horwell *et al.*, 2013) and the presence of secondary clay minerals is postulated as the possible instigator of haemolysis of these quarried volcanic samples (as detailed in Chapter 5). The elevated haemolysis among the quarried volcanic samples (Chapter 5, Section 5.4.4) may thus be due to mineral phases that are not present in freshly erupted volcanic ash. One possible explanation is that secondary clay minerals are the instigators of haemolysis in the quarried samples (Chapter 5, Section 5.4.4). Clays tend to be rich in aluminium and previous work on the Flat Top deposit has revealed secondary mineralisation of chlorite, smectite and illite groups (Nicholson *et al.*, 2000), all of which also contain iron.

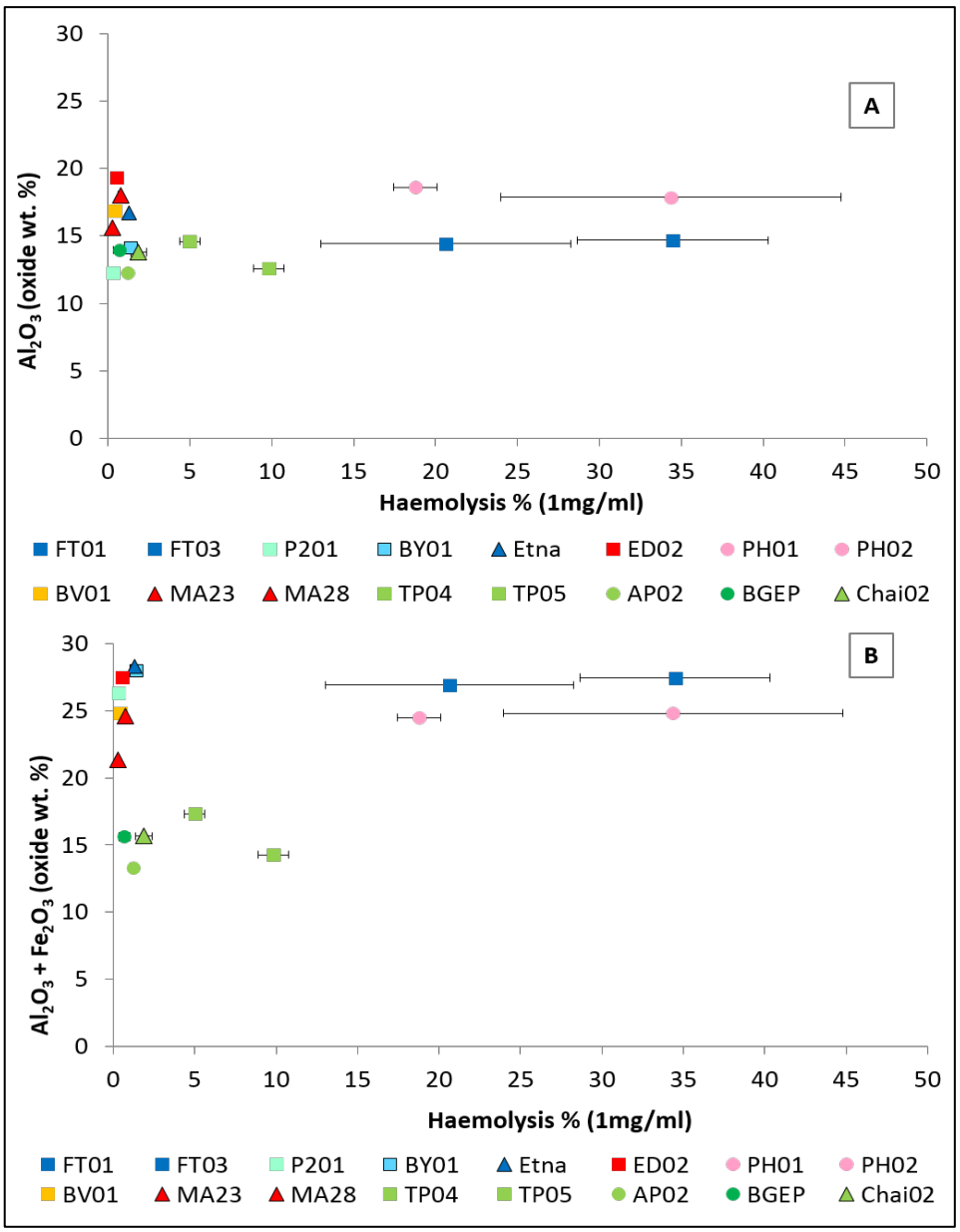

Figure 7.8 A) Al_2O_3 and B) $Al_2O_3 + Fe_2O_3$ (oxide wt.%) contents (from XRF) versus haemolysis % (1mg/ml). Error on haemolysis is standard error of the mean (σ/√N) (N=3).

Given that clays have substantial Al_2O_3 and some are also iron rich, in order to investigate whether clays are contributing to the haemolysis results, Figure 7.8 plots haemolysis versus the bulk contents of Al_2O_3 and with Al_2O_3 and Fe_2O_3 combined (using data from Chapter 4, Section 4.4.1, and Chapter 5, Section 5.4.3). No correlation is observed between Al_2O_3 and haemolysis (Figure 7.8 A). Samples with elevated haemolysis e.g. those from Te Puke (TP04 and TP05) and from Flat Top (FT01 and FT03) contain similar amounts of Al_2O_3 (between 13 and 15 wt.%), but haemolysis values between 5 and 35% (1mg/ml). At the same time, the two sets of most haemolytic samples, from Te Puke and from Phoenix (PH01 and PH02), show similar ranges in haemolysis (c. 18-35% (1mg/ml)), but with different aluminium contents (c. 14 and 18 wt.% for Flat Top and Phoenix; Figure 7.8 A). A weak positive correlation is suggested for Al_2O_3 + Fe_2O_3 and haemolysis (Figure 7.8 B) for the haemolytic samples from Flat Top, Te Puke and Phoenix. Samples with low haemolysis are provided for comparison; however, no correlation is expected.

The lack of positive correlations may reflect the fact that the Al_2O_3 and Fe_2O_3 contents from bulk compositions are determined by the primary mineral phases (plagioclase feldspar mainly for aluminium, and pyroxene and amphibole mainly for iron) and that these are not necessarily proportional to the smaller contributions from secondary clays. For a definitive test, future analyses will need to isolate the contributions from the clay fraction and the crystalline silica and compare these with the sample haemolysis. This might be achieved by running haemolysis on the complete subsample, as as well as, on the separated clay fraction and on the separated crystalline silica. Clay could be separated by centrifugation with addition of a de-flocculant (Section 5.3.6) and crystalline silica by picking and a heavy liquid separation technique (with subsequent acid washing to ensure any remaining heavy metals were removed from surfaces to avoid occlusion).

7.3.3 Implications

Even in combination, the data for surface area and crystalline silica do not yield clear indications of a likely influence on particle toxicity. This is probably because crystalline silica itself is highly variable in its toxicity. The underlying reason for the variability is

difficult to constrain, not least because the exact mechanism by which this toxicity is instigated has yet to be identified (Fubini *et al.*, 2001, Meldrum & Howden, 2002). Several potential factors regarding surface functionalities and modifications of crystalline silica may affect a sample's cytotoxicity, either on their own or in combination. These factors include: the presence of impurities, such as carbon (Ghiazza *et al.*, 2013) or aluminium (Duffin *et al.*, 2001, Stone *et al.*, 2004); the occlusion of the surfaces by other adhering minerals or salts; the piezoelectric charges resulting from freshly cleaved Si-O bonds (Williamson *et al.*, 2001); and the heat treatment of particles which leads to annealing of surfaces (Fubini *et al.*, 1999) and may result in hydrophobicity (Bolis *et al.*, 1991). The grinding processes in quarries may produce particles with freshly cleaved Si-O bonds, unlike samples which have resided in the environment for longer and are weathered (such as those in a stockpile). The piezoelectric charge was not investigated in this study and so is suggested as a useful parameter to determine in future work (Chapter 8). The heat-treatment of particles which may anneal particle surfaces is similar to that employed in processing the quartz-rich sandstone MSR into the cristobalite sample MSCr; however, as these were the only samples to undergo this process and are not volcanic in origin, the effects of heat treatment were not examined as part of this study.

The bulk content of Al_2O_3 and Fe_2O_3 by XRF cannot be used to indicate the potential contribution of clays to haemolysis. Whilst XRF is useful for determining the bulk composition of magma types, it does not reveal which minerals contain the elements of interest. Clays are the result of weathering, however, their Al_2O_3 contribution to a sample's bulk chemistry may be comparative to that from primary mineral phases, hence, it is not possible to determine whether the signal is from primary or secondary mineralisation.

Sample toxicity, as demonstrated in the haemolysis assay, involves a number of parameters with complex and interacting relationships. It is thus difficult to separate out and determine the influence of a single parameter to the exclusion of others. The controls on haemolysis are likely to include both the crystalline silica content and the surface area, but are also likely to be influenced by the surface functionality of the crystalline silica itself, as well as the potential presence of other phases such as clays.

7.4 Relationship between deposited and airborne fractions

To determine likely levels of non-role specific dust exposure, ambient monitoring was undertaken of airborne PM10 concentrations (Chapter 6) and an 8-hr TWA average calculated (Table 6.6). The aim of this monitoring was to try to determine whether any particular area within a quarry had greater exposure (in terms of PM10 concentration) than others. Samples of deposited material were collected for analysis from various parts of the quarry, and their <10µm content was determined as part of physicochemical characterisation (Section 4.4.2). Many of the deposited samples were collected from the same areas where ambient airborne monitoring took place therefore, it would be useful to know if one can use the proportion of <10µm material in deposited dust to determine how elevated airborne concentration of PM10 may be. Figure 7.9 plots the <10µm (cu. vol.%) material of samples taken from three quarry areas: the quarry floor near the roadside, the processor and post-blasting, against 8-hr TWA average of PM10 concentrations taken at similar locations.

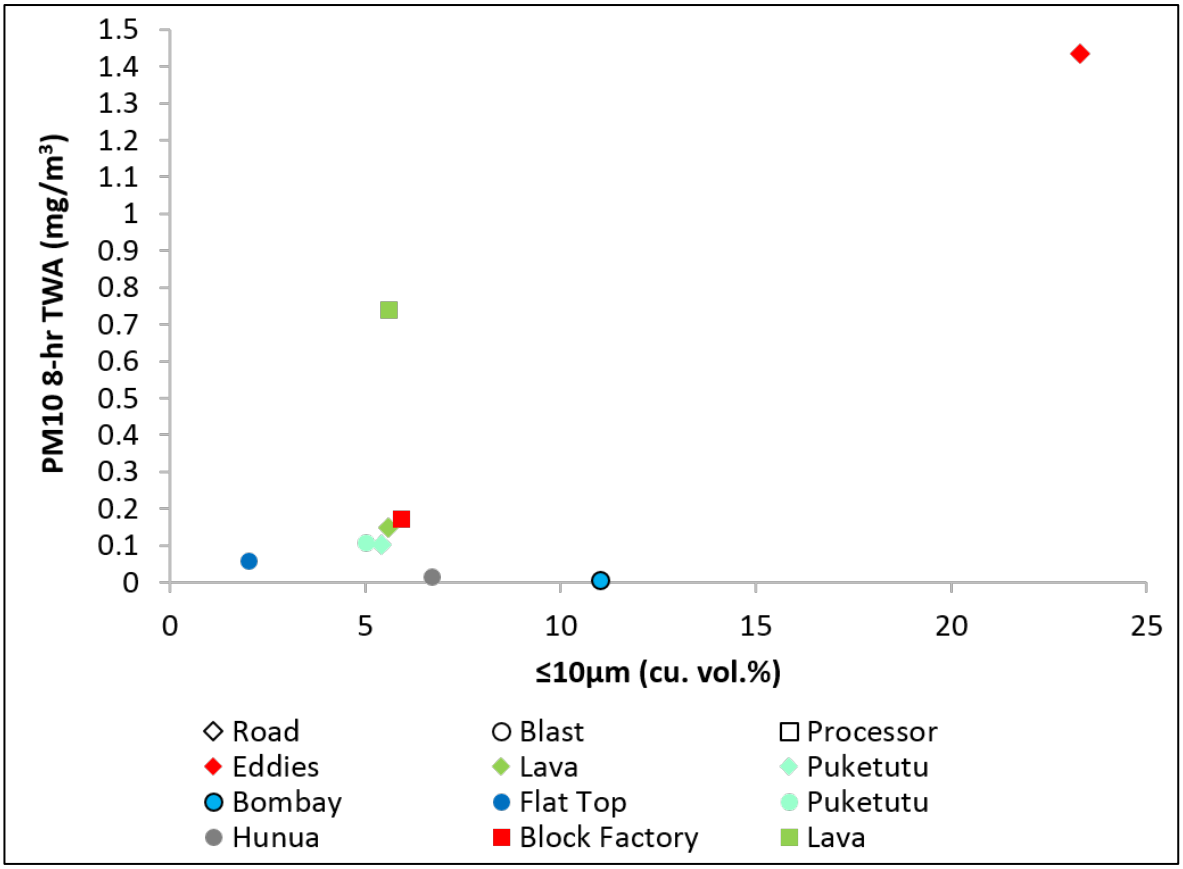

Figure 7.9 The <10µm (cu.vol.%) proportion of samples versus the concentrations of PM10 8-hr TWA (mg/m3) at three quarry areas: road (diamonds), blast (circles) and processor (squares).

There is no correlation observed between the quantity of <10µm material in deposited samples versus the 8-hr TWA average of PM10. Comparisons of the average proportion of <10µm material across the same types of deposited samples was variable and it was not possible to determine differences in these averages (Figure 4.9); furthermore, patterns could not be inferred for airborne exposure in different areas of the quarries from the limited data set. The variability in these datasets may contribute to the lack of correlation observed here; however, it may also be due to differences in airborne dust and accumulated dust arising from the environmental conditions at the time of sampling, e.g. wind, relative humidity (discussed in detail in Chapter 6, Section 6.3.4).

Several factors therefore are likely to influence the airborne concentrations of PM10 in a quarry and these cannot be determined on the basis of the proportion of <10µm of dusts deposited in a similar location.

7.5 Holistic appraisal of all health-pertinent parameters

As outlined in 7.2 and 7.3, the influence of a single physicochemical parameter upon surface reactivity and haemolysis can be difficult to determine, particularly when several parameters are likely to be working in conjunction and exerting greater and lesser influences. It may be helpful, therefore, to consider as many parameters as possible simultaneously, in order to observe any patterns between physicochemical parameters and resulting reactivity and toxicity. This is difficult to achieve graphically, therefore Table 7.1 qualitatively ranks all of the volcanic quarry samples studied, under different headings, each representing the different analyses. As the purpose of this table is to observe any individual patterns between the volcanic quarries, the ash comparisons and non-volcanic quarry samples are excluded from the ranking. The samples are ranked from highest/most to lowest/least for each category. It is important to note, however, that this is a qualitative ranking for illustrative purposes and the prominence of one sample over another across any (or several) categories should not be interpreted as indicating a greater likelihood of potential hazard, nor should any safety-critical dust management decisions be made on this basis.

Table 7.1 Qualitative ranking (high to low) of samples according to health-relevant parameters for the <1mm fraction (overleaf). Mafic (blue), Intermediate (red), Felsic (green).

Quantity of <10µm	Surface Area m^2/g	Total crystalline silica content (wt. %)	Bulk Fe content (oxide wt. %)	Bulk Si content (oxide wt. %)	Total Fe^{2+} and Fe^{3+} released (after 7 days)	Hydroxyl Radical Generation (30 mins)	Haemo-lysis % (at 1mg/ml)
1 BY01	1 FT03	=1 PH01	1 BY02	1 AP04	1 P205	1 JN01	1 FT03
2 ED01	2 FT01	=1 PH02	2 BY01	2 AP03	2 P201	2 ED02	2 PH02
3 LB01	3 TP04	=1 Obs03	3 P201	3 AP02	3 BY01	3 P205	3 FT01
4 PH01	4 PH02	=2 ED02	4 P203	4 AP05	4 FT01	4 BY01	4 PH01
5 P205	=5 BY01	=2 BV01	5 FT03	5 AP01	5 PH01	5 P202	5 TP05
6 TP04	=5 TP05	3 BV03	6 FT01	6 TP05	6 FT03	6 BV01	6 TP04
7 BV02	6 PH01	4 TP04	7 ED01	7 BGEP	7 ED02	7 PH01	7 BY01
8 TP03	7 BGEP	5 TP05	8 ED02	8 LA01	8 BV03	8 BV03	8 AP02
9 P201	8 P201	6 AP02	9 BV01	9 LA04	9 BV01	9 LA01	9 ED02
10 BGEP	9 BGRP	=7 FT01	10 BV02	10 LA02	10 JN01	10 AP02	10 BV03
11 BY03	10 AP02	=7 FT03	11 PH02	11 BGRP	11 PH02	11 FT01	11 BV01
12 BV01	11 P205	=7 P201	12 AT03	12 LA03	12 TP05	12 BGRP	12 P201
13 TP02	12 BV01	=7 BY01	13 PH01	13 TP04	13 TP04	13 BGEP	
14 PH02	=13 BV03		14 AT04	14 AT04	14 BGEP	14 PH02	
15 BY02	=13 JN01		15 TP04	15 AT03	15 AP02	=15 FT03	
16 Obs03	14 ED02		16 TP05	16 PH02		=15 TP05	
17 FT01			17 BGEP	17 BV02		16 TP04	
18 BY04			18 BGRP	18 BV01			
19 LA02			19 LA01	19 PH01			
20 AP01			20 LA04	20 ED01			
21 AT04			=21 LA02	21 ED02			
22 TP01			=21 LA03	22 FT01			
23 BF02			22 AP01	23 FT03			
24 LA01			23 AP05	24 BY01			
25 BF01			24 AP02	25 BY02			
26 P204			25 AP03	26 P203			
27 BV03			26 AP04	27 P201			
28 LA04							
29 AP02							
30 AT01							
31 P203							
32 P202							
33 LA03							
34 ED02							
35 AP05							
36 JN01							
37 AP04							
38 TP07							
=39 FT03							
=39 TP05							
40 TP06							
41 AP03							
42 FT02							
43 BV04							
44 AT03							

Table 7.2 Qualitative ranking (high to low) of samples according to health-relevant parameters for the ≤10µm fraction

Aspect Ratio	Crystalline Silica Content (wt.%)	Haemolysis (1mg.ml)
1 BY01	1 PH01	1 PH01
2 TP05	2 PH02	2 PH02
3 FT01	3 TP04	3 TP04
4 TP04	4 FT03	4 TP05
5 Obs03	5 FT01	5 FT02
6 PH02		6 FT01
7 FT02		7 BY01
8 PH01		8 Obs03

As can be seen from Table 7.1 for the <1mm samples and Table 7.2 for the size separated ≤10µm samples, no single samples feature prominently across all categories. Sample FT03 in Table 7.1, for example, exhibits a comparatively high surface area and commensurately high haemolysis, it also ranks comparatively highly for iron release and free radical generation; however, it does not contain a large proportion of the <10µm fraction (ranked joint 39th) and therefore only a small proportion of this sample overall is likely to penetrate the lungs of quarry workers if it becomes airborne in the quarry. Sample BY01 contained the greatest quantity of <10µm fraction and also ranked highly for iron release and radical generation, however, quantification of these factors alone is not enough to determine whether this sample is of potential risk as, although the hydroxyl radical generation is indicative as a chemical test, it does not replicate exactly what may happen in the lung which is a dynamic system and which features components which may oxidise or reduce the surface iron ions.

In Table 7.2, samples from PH, TP and FT, ranked in the same order for crystalline silica content and for haemolysis. This does not, however, suggest that haemolysis is commensurate with crystalline silica content; especially as the FT samples contain only around 1 wt.% crystalline silica. Whilst it is possible that for the samples from Phoenix and Te Puke quarries (PH01 and 02, and TP04 and 05, respectively) the crystalline silica is a contributing factor, there are likely to be other factors also involved, such as the presence of clays, the surface area of the sample and other potential factors such as the surface functionalities of the silica (as described in 7.3.3).

The type of ranking shown in the table enables a rapid assessment of which samples have characteristics that are known to influence toxicity, and to aid in establishing which

should undergo further analysis. Such further analysis may include assays on human cells, such as the monocytic THP-1 cell line which is commonly used as a model for phagocytosis (where cells engulf particles) or with lung epithelial type 1-like (TT1) cells, which have been previously used to determine toxicity of volcanic particulate including that which is actively quarried (Damby, 2012, Damby *et al.*, 2013).

7.6 Challenges and Limitations

The determination of both the influence of individual physicochemical parameters on reactivity and toxicity, and the holistic appraisal of overall hazard are confounded by several factors. These include: the differences between laboratory standards and field samples, the number of samples obtained from individual quarries and their comparability, and the use of the <1mm fraction to determine potential airborne hazard; and are discussed in more detail below.

7.6.1 Quantity of samples and comparability

There are some cautiously inferred potential correlations between the parameters studied here, which might possibly have yielded stronger relationships had more samples been studied from each deposit. Samples here were selected on the basis of representing different stages of the quarrying process in order to provide as accurate an overall impression of the airborne hazard as possible. The trade-off to this is that sample types are not always directly comparable, in that a sample drawn from raw material may exhibit different physicochemical properties. Such differences can be difficult to account for with only a few different samples types per quarry. If there is little variation in parameters of samples taken from the same quarry, however, then additional samples will not affect the overall trend, but will present the same lack of correlation as shown here albeit with more data points which would strengthen confidence in the interpretations.

7.6.2 Use of the <1mm fraction versus use of the ≤10µm fraction

The comparisons between different parameters made here are based upon the results of analyses conducted upon the <1mm fraction sieved from the bulk and may differ substantially from the results which would be elicited by a lung-pertinent fraction. Horwell et al., (2003) found that ash plumes produced by PDCs which result from dome collapse events (known also as co-PDC ashfall) are enriched in cristobalite in the <2µm fraction; this is likely to be a consequence of size and density fractionation as dome rock is fragmented within PDCs (Horwell *et al.*, 2001). It is likely, therefore, that samples of dust taken from PDCs related to dome collapse events (such as the PH samples from Montserrat, for this study) may show differences in crystalline silica content between the <1mm sieved fraction and the <10µm fraction, as demonstrated in Chapter 4. The hydroxyl radical data (as shown in table 7.1) is expressed as a function of surface area, as it is known from laboratory studies that surface area influences reactivity. It was not possible to determine the surface areas of the separated <10µm fraction for this study, therefore it must be noted that the hydroxyl radical generation and iron release of the two different size fractions may differ greatly. Horwell et al. (2003) compared several samples of respirable and bulk ash and found that respirable samples had a higher surface area and displayed increased reactivity compared to their bulk counterparts.

7.7 Conclusions

Natural mineral dusts are complex mixtures of minerals with varying characteristics within individual subsamples even from the same quarry. This study has shown that hazard assessment through physicochemical characterisation is challenging with health-pertinent parameters not correlating with disease mechanisms in the laboratory. The natural variation in the samples precludes the control of confounding factors. The comparisons between different health-relevant parameters discussed here, reveal that separating out a single factor and its individual influence is a complex process due to the inter-relatedness of different parameters which serve in combination to influence particle toxicity and potential airborne hazard.

Particle characterisation, using parameters (such as described in this study in Chapter 4) is a useful first-order tool in determining which sample types may have the *potential* to pose a hazard, however, they do not serve to quantify the hazard which

might be posed to the respiratory health of quarry workers. Quantifying hazard is further complicated by the fact that 'safe' thresholds for the different parameters do not exist and therefore compounding factors such as the variability of crystalline silica content is difficult to account for. Following this first-order characterisation, some samples may be selected for further toxicological and physicochemical analysis, notably samples which score highly across several health-relevant parameters, for example:

1) Mafic samples which contain high levels of respirable material, large surface areas, release large amounts of iron and generate large quantities of hydroxyl radicals.
2) Intermediate and felsic samples which contain high levels of respirable material, large surface areas, are composed of elevated levels of crystalline silica and elicit a high haemolytic response (once influence from secondary mineralisation or other factor(s), has been eliminated as a potential driver of haemolysis).

Such physicochemical investigations may include determining the piezoelectric properties of samples rich in silica and creating high haemolysis and their surface hydrophilicity/hydrophobicity and further investigation of the surface characteristics of particles e.g. leachable elements. The cytotoxicity of particles may also be tested using assays with human lung cells. These suggestions for further work are discussed in Chapter 8.

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Chapter 8 – Conclusions

8.1 Synthesis of Research

The primary aims of this thesis were to investigate, for the first time, the potential health hazard of dust specific to a range of quarried volcanic deposits and to test whether volcanic ash can be used as a reliable analogue for quarry dust (Chapter 1, Section 1.2). This chapter synthesises the key results and presents recommendations for enhancing the integrity of future investigations.

8.1.1 Holistic Hazard Appraisal: Summary of Findings

A wide range of volcanic deposits are quarried, including: massive lava flows, ash-fall deposits, pyroclastic density currents and domes, with an associated range of industrial applications. The modes of extraction and processing yield a range of sample 'types'. The representative types sampled here, which had bulk chemical compositions from basalt, through andesite and dacite, to rhyolite, displayed large variations in physicochemical characteristics, often between samples from the same deposit (Chapter 4). For example, samples of drilled mafic lava flows commonly contained greater amounts of the <15µm size fraction than other types; samples from quarries of andesitic to rhyoltic composition contained appreciable quantities of health-pertinent material and those from lava domes were also found to contain the highest levels of crystalline silica.

Iron release was found to be greatest in samples of mafic origin, although this was not concomitant with the generation of hydroxyl radicals (Chapter 5). From this alone, however, it is not possible to determine whether dust particles from mafic deposits pose a potential hazard. Whilst radical generation is known to contribute to inflammation and other precursors to disease, it is not linked with a particular disease endpoint. El Ghawabi et al. (1985) linked exposure to dust from basalt quarrying with incidence of pneumoconiosis, but did not identify a mechanistic link. Further investigation is warranted, therefore, particularly as the drilled lava samples studied here contain large quantities of respirable material.

Levels of haemolysis (Chapter 5) were found to be elevated for six of the studied samples from mafic, intermediate and felsic quarries. Four of these contained appreciable levels of crystalline silica, whilst all six contained clays. Determining the individual contribution to haemolysis of crystalline silica and clay is a key next-step (Section 8.3).

The exposure of quarry workers was found to be within occupational exposure limits at all of the locations studied (Chapter 6) during the limited field season. These are based on 8-hr time weighted averages which, in turn, are based upon an eight hour shift, five days a week. Where shift patterns exceed this and when workers are also exposed to volcanic ash, such limits may not be appropriate and therefore mitigation measures are particularly relevant. Dust management also varied among quarries, with more comprehensive strategies employed by larger multi-national companies compared to smaller, independent enterprises.

8.1.2 Testing of volcanic ash as a suitable analogue

A suite of volcanic ash samples (selected for their broad comparability by magma and eruption type) was analysed alongside the volcanic quarry samples, as both a benchmark for comparison and to determine whether ash could be used as a suitable proxy for future investigation of potential hazard. The majority of analyses were undertaken on the <1mm fraction so that direct comparisons could be drawn with results from the published literature.

Overall, volcanic ash is a limited analogue for quarry dust, despite comparisons between similar magmatic composition and eruption style. There were some similarities in the physicochemical characteristics, mainly limited to grain size distribution and morphology. There were few similarities in the surface reactivity tests because volcanic ash released more iron and generated more radicals than quarry dust. In the haemolysis assay, both volcanic ash and quarry dust showed negligible results (with the exception of the six quarry samples which exhibited elevated haemolysis). This does not necessarily mean that their toxicity is similar, because haemolysis is a first-order indicator of toxicity and does not represent the actual reactions of particles within the lung.

There is a dearth of epidemiological and clinical studies in relation to the potential toxicity of volcanic ash. Further studies may elicit greater understanding of the health-relevant parameters involved and, therefore, volcanic ash may eventually emerge as a more viable analogue.

8.2 Suggested Further Work

A limitation of this study is that the use of the deposited <1mm fraction may not be completely representative of the potential hazard posed by the airborne respirable fraction of the same material. For evaluating respiratory hazard, the collection of bulk samples deposited on surfaces (quarry floor, processor, stockpile) is less representative than the collection of dust particles from the air; however, use of a high-volume impactor, which collects airborne dust, is unlikely to yield enough sample for an in-depth physicochemical analysis. Furthermore, the use of a high-volume impactor does not allow for representative sampling of different dust types (e.g. freshly extracted, processed or weathered) which is crucial to determining hazard, as not all sample types will exhibit the same toxicity (Mazziotti *et al.*, 2004). High-volume collectors could, therefore, be employed alongside the collection of deposited samples and determinations made of any likely differences in characteristics between the airborne and deposited fractions. Challenges of obtaining enough sample for characterisation can be addressed through sample re-use following non-destructive analyses – for example, dust particles characterised for surface area by N_2 adsorption can subsequently be used for XRD analysis to investigate mineral phases of interest.

8.2.1 Physicochemical characterisation

Further physicochemical analyses may help to constrain the variation displayed by the studied samples. No relation was observed between surface area and grain size, possibly due to the porosity of the samples. Determining porosity (e.g. by mercury intrusion porosimetry) may help to explain interactions between surface area and exhibited reactivity and toxicity. The hydrophilicity (a measure of water attraction resulting from charge polarisation) of dust particles can also be an important consideration, because hydrophilic mineral particles demonstrate the strongest interaction with biological molecules and are pre-disposed to protein adsorption and denaturisation, as well as cell-surface adhesion which may lead to cell injury (Fubini & Otero-Areán, 1999).

The determination of piezoelectric and electrokinetic properties may also contribute to better understanding the potential hazard. Radical generation may occur as a result of piezoelectric effects when rocks containing crystalline silica are fractured in a quarry (by extraction or processing), producing broken Si-O bonds that result in ‘dangling

bonds' or electrically charged surface species (see Chapter 5, Section 5.5.1 and Figure 5.1). Quantifying the piezoelectric effects of quarry dusts containing quartz, cristobalite and tridymite may help to explain any resultant toxicity (Williamson *et al.*, 2001), especially where quarrying creates freshly cleaved particle surfaces. Analysis should also be carried out on samples freshly ground in the laboratory in order to better simulate the quarry environment.

The electrokinetic or zeta potential (ζP) reflects the magnitude of attraction or repulsion between particles and can also influence toxicity. In haemolysis, for example, a difference can exist between the dispersion medium and the stationery layer of fluid which is attached to the particle. This is an effect which can be replicated in the lungs with surfactant as the dispersion medium. The ζP is known to be influenced by pH and both expanded and raw perlite have been found to remain negatively charged in a pH rage of 3-11 (Dogan *et al.*, 1997). Cho et al. (2012) found that haemolytic activity can be lost and recovered depending on the charge of the surfactant corona, highlighting that knowledge of the surface functionalities is an important component of investigating haemolytic activity and likely subsequent reactivity in the lung.

Crystalline silica is typically haemolytic, as demonstrated by the industrial silica samples tested in Chapter 5. However all of the samples that exhibited elevated haemolysis were found to contain clays whilst only four contained appreciable crystalline silica. Further testing could determine whether this crystalline silica is contributing to the haemolytic effect by treating silica-rich samples with aluminium lactate. Duffin et al. (2001) found that treating a DQ12 quartz standard (which also contains small contaminations of the clay kaolinite (Robock, 1973)) with an aluminium lactate salt did not affect the size or aggregation of particles, but did result in a 12-fold reduction in haemolysis compared to untreated quartz. The exact interaction between aluminium and the particle surface is unknown, but it is postulated that under acid conditions the aluminium inserts into the place of silicon in the quartz crystal lattice (Duffin *et al.*, 2001, Fubini, 1998).

Leachates could also usefully be examined to determine the trace elements capable of being leached from the surface of the particles or the minerals capable of being dissolved. In the quarry environment, leaching might occur whilst material is being washed during processing or from rainfall on stockpiles. Removal of these elements may

either reduce the toxicity (if trace elements or minerals on the surface might adversely influence toxicity (Cronin *et al.*, 2003, Witham *et al.*, 2005)) or increase toxicity if their removal reveals a more toxic 'core' to the particles. A leachate solution which simulates lung fluid (e.g. Gamble's solution) would also be appropriate as this would reveal what the lung cells may scavenge from the surface of the dust particles and what reactions may subsequently occur.

8.2.2 Toxicity testing

Whilst haemolysis is a useful first-stage test to identify the potential toxicity of particles (on the basis of their ability to cause cell lysis), it is not representative of biological interaction within the lung. Samples which exhibit haemolysis should first be tested (as described above, Section 8.2.1) to determine whether the lysis relates to crystalline silica or is a false positive, based upon secondary minerals such as clays, and subsequently analysed using lung specific tests. These involve cultured epithelial and macrophage cells to assess cell viability and cytotoxicity through measurement of cell metabolic activity and stress. A further experiment could investigate pro-inflammatory response to quarry dusts, by measurement of the production of inflammatory markers. Such tests have previously been carried out on volcanic ash (e.g.(Damby *et al.*, 2013, Wilson *et al.*, 2000).

8.2.3 Dust monitoring and management in quarries

Dust monitoring of PM10 levels at a quarry ought to be carried out over periods of several weeks throughout the year. In this way, many specific variables can be accounted for, including seasonal changes in weather, natural variation in deposits (pertaining to rock strength and moisture content), rate of production, types and numbers of vehicles employed, and dust mitigation activities, such as the use of water carts.

Investigations into occupational risk perception and tailored risk communication, may benefit quarries where managers and employees are uncertain of the respiratory risks posed and feel ill-equipped to make decisions regarding non-mandatory PPE.

8.3 Final Conclusions and Recommendations

Despite decades of research into dust hazard, from clinical and epidemiological studies to specific physicochemical and toxicological analyses, quarrying remains an occupation with one of the world's highest levels of morbidity and mortality. This study has revealed that, at least for quarries excavating volcanic deposits, a generalized hazard assessment cannot be undertaken for two main reasons. First, the quarried materials cover such a broad range of magma compositions and deposit types that it is not possible to apply results to a single, generic 'volcanic' category. Second, even within the same quarry, or between quarries excavating similar types of deposit, the variation of physicochemical characteristics can be too large for a meaningful generalisation based on the type of deposit or its mode of emplacement. As a result, site-specific studies should be undertaken and repeated as necessary in line with the size of the deposit being extracted and the concomitant life of the quarry, because no deposit will be completely homogenous and variations in its characteristics can be expected as quarrying proceeds.

In-depth analyses of a range of physicochemical and toxicological characteristics at every volcanic quarry is unlikely to be warranted or practical. Monitoring methods which exist at quarries extracting silica-rich deposits (e.g. Hunua, Moneystone), such as regular air quality monitoring coupled with assessment of crystalline silica content, may be appropriate for some volcanic quarries where material is likely to be fine-grained and rich in crystalline silica (e.g. from dome-forming settings or rhyolitic lavas and pumices rich in quartz). Although studies of the toxicity of volcanic ash have yielded negative results (e.g., (Berube *et al.*, 2004, Damby *et al.*, 2013, Horwell *et al.*, 2013, Wilson *et al.*, 2000), ash cannot automatically be assumed to be a reliable analogue of quarry dust (Section 8.1.2). The potential toxicity of volcanic particulate from quarries can thus only be determined conclusively with targeted epidemiological and clinical studies. Similarly, until more is known about the possibility of a disease endpoint related to iron release, quarries which drill iron-rich lavas might potentially adopt a precautionary approach to reduce their hazard by removing the piles of drilled fines (from the rock surface) prior to blasting; indeed, in some cases this can be economically advantageous (Mitchell, 2007).

The appropriateness of OELs warrants further investigation in areas where workers are either exposed to quarry dust during longer shift patterns, or exposed at the same time to both volcanic quarry dust and volcanic ash. Effective dust management,

such as the use of water carts and effective risk communication with employees, is particularly germane in such environments, especially for smaller companies without formal procedures for dust management.

In conclusion, it has been shown here that volcanic quarries produce a range of dusts that, owing to their variation in composition and in health-pertinent characteristics, are likely to vary in their potential health hazard. These outcomes are currently under-researched so further work is necessary before detailed recommendations can be made. Until the further studies have been completed, a precautionary approach to hazard assessment is recommended for quarry practices, especially where the dust is particularly fine grained or potentially rich in crystalline silica. Simple precautions include regular dust suppression and measures to reduce the inhalation of dust. Reducing dust at source is always desirable and more appropriate OELs, coupled with increased awareness, would better inform workers regarding decision-making in relation to non-mandatory respiratory protective equipment.

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